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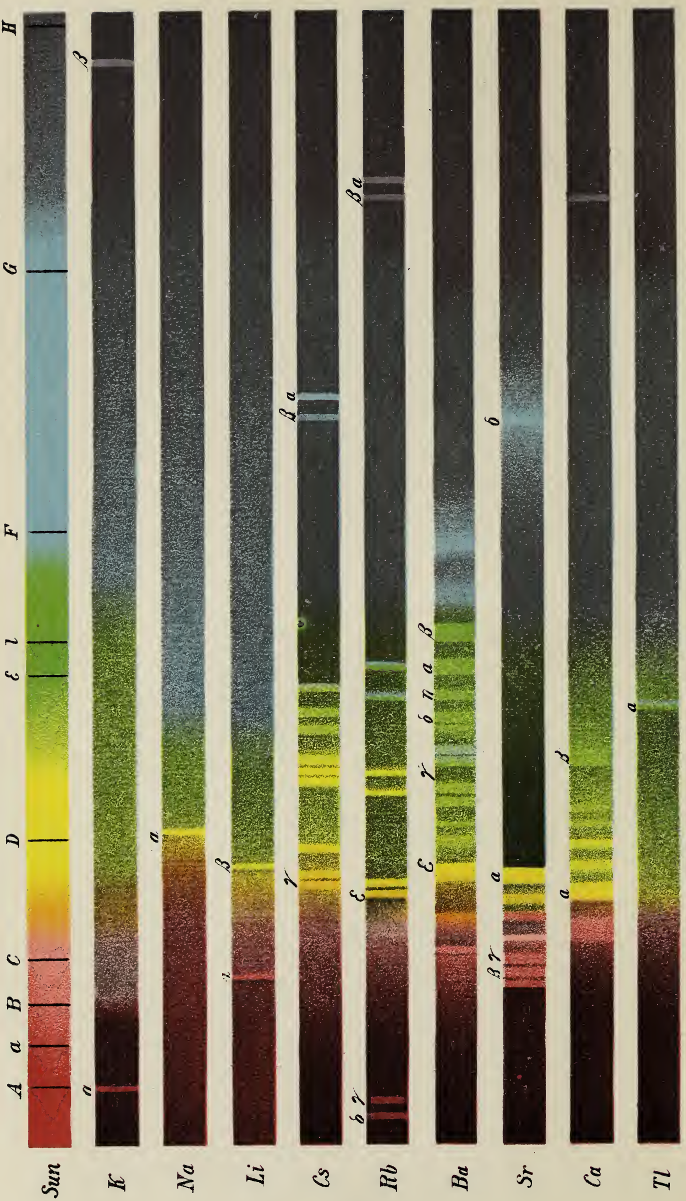

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ECLECTIC EDUCATIONAL SERIES.

THE ELEMENTS

OF

CHEMISTRY

INORGANIC AND ORGANIC

BY

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Presented to
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PREFACE.

THIS work is intended as a text-book, not as a manual for reference. The author has endeavored to select such chemical phenomena as represent the cardinal principles of the science, giving preference to those which are easily reproduced by the student, and which enter into the affairs of common life. To attain this end, he has omitted many excellent experiments which require the use of expensive apparatus, and has substituted others which, if less "classical," are of easier application.

The engravings represent well-fashioned apparatus; but no one ought to be deterred from attempting an experiment because he has not the exact shaped figure. Any drug-store or kitchen will afford bottles and tumblers, which may be used in place of flasks and beakers. In some way, the experiments ought to be tried. Glass tubing, rubber tubing, and good corks are the first requisites, and are easily obtainable. The most essential thing in experimenting is the experimenter. He should know (1) what he proposes to do; (2) what are the means at his command; and (3) how he intends to use them. He must bear in mind that a Chinese fidelity is not required — *e. g.*, that one alkali may replace another, or that corresponding salts may be substituted one for another as occasion requires. Nevertheless, he must remember that Chemistry is exact in her methods; (1) that careless manipulation will not secure good results; and (2) that such words as neutral, acid, basic, excess, must not be neglected.

As regards nomenclature, the author has endeavored to follow as closely as possible, in a work of this size, the rules of the London Chemical Society. Old and well-known names have been retained because of their common use.

As regards notation, it must be borne in mind that all formulæ are alike subject to change. No greater mistake can be made than that any formula (except a binary) tells the whole truth about a molecule, or that any formula which correctly represents the percentage composition of a substance may not be, at times, available in fixing in the mind of the student the fact to be remembered. The author has, therefore, used the formula that appeared convenient at the time; and feels that an experience of twenty years' teaching warrants him in advising his fellow-teachers not to attempt to place theory above practice. The use of theory is to enable one to generalize known facts and predict new ones; the business of teaching is to enable the student to master facts, principles, and laws already ascertained and established.

The Science of Chemistry is not an easy one to master; but it will well repay careful study, not only by reason of the evident importance of the facts it presents, but also as regards its special discipline in Education. It is hoped that the selection of facts herein presented are such as will be found useful in themselves, and also well calculated to develop the principles upon which the Science is founded.

The present edition has been thoroughly revised, and has also been enlarged by the introduction of a dozen chapters treating of Organic Chemistry.

The author's thanks are due to Mr. Curtis C. Howard, of Columbus, and to Mr. Pliny Bartlett, of Cincinnati, for material assistance rendered during the passage of the book through the press. If any errors are found which have escaped their very careful proof-reading, the author will be obliged to any one who will take the trouble to point them out.

Columbus, Ohio, *Nov.* 1, 1884.

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CHEMISTRY.

CHAPTER I.

LAWS OF CHEMICAL COMBINATION.

1. Many common phenomena are the results of chemical action. If iron filings are moistened and exposed to the air, they become changed to the orange-red powder called iron rust. The iron loses its luster, its tenacity, its property of being attracted by a magnet; in fact, it loses its identity, and we recognize iron rust as a different kind of matter from iron. When a body is so altered that its physical properties disappear, and a new kind of matter has been formed, a chemical action has taken place.

The constituents of the atmosphere are continually acting upon the substances which are found on the surface of the earth, and are effecting in them chemical changes. Among these changes are the decay of leaves, the burning of wood and candles, the rusting of iron, and the souring of milk and cider. As the result of these actions new bodies are formed, which are essentially different from the original substances.

2. The atmosphere is so constantly engaged in producing chemical changes that we must first determine what its constituents are.

Experiment 1.—Place in a glass beaker a freezing mixture of ice and salt. After a little, the outside of the dish will be covered with moisture, which in process of time will collect in drops of water. See **Exp. 39.**

The atmosphere, therefore, contains water which is usually disseminated through it as an invisible vapor. The quantity of aqueous vapor in the air is always small, and of no constant proportions. The average is 1.4 per cent by volume, or 0.87 per cent by weight.

The vapor of water may be removed from air and other gases by passing them through vessels containing calcium chloride or sulphuric acid or quicklime.

Exp. 2.—Expose a lump of quicklime in an open dish. After a few days it will crumble to a light powder. This is air-slaked lime. The lime has combined with the water in the air and has formed a compound which is called calcium hydrate.

After a longer exposure the lime will combine with another constituent of the air called carbonic acid, or carbonic anhydride, to form calcium carbonate. If old mortar be dropped in a dilute acid, it will *effervesce* or give off bubbles of the same gas, which has been obtained by long contact with the air. Carbonic anhydride forms usually four parts in 10000 of the atmosphere, but even this relatively small quantity is essential to the growth of plants.

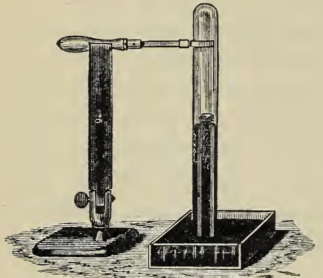

FIG. 1.

Free carbonic anhydride may be removed from air or other gases by passing them through a solution of potassium hydrate, or through "milk of lime."

Exp. 3.—Invert a glass tube closed at one end and filled with dry air in a basin containing mercury. Wrap a piece of clean sodium in filter paper, and bring this within the tube. After a few days the volume of the air will contract, and the mercury will rise and fill about one-fifth of the tube. Now, close the tube with the thumb, and remove it from the basin. Test the gas remaining by plunging an ignited splinter of pine within the tube. The blaze will instantly be extinguished.

The gas that remains, and that will not support combustion, is called *nitrogen.* It constitutes 79.19 per cent of dry air by volume, or 76.86 per cent by weight.

The constituent of the air which has been removed, is called *oxygen.* It constitutes 20.81 per cent by volume, or 23.14 per cent by weight of dry air. Open the paper in which the sodium was wrapped. The metal will be seen to be coated with a dry powder, which is called sodium oxide (Na_2O). It has also gained in weight.*

Oxygen is the efficient agent in producing the changes mentioned in § **1.** The nitrogen is inert, and its principal use seems to be to dilute the oxygen and diminish the rapidity of its action. When a metal corrodes or rusts in the air, it does so by combining with oxygen. The process is called *oxidation*, and the product formed by *oxidizing* a metal is called an *oxide* of that metal.

The air contains also very small traces of ammonia and other vapors, but these may be neglected for the present. All these constituents of the air are merely *mixed* together and are therefore readily separated. Water, for instance, will absorb from the air a greater proportion of oxygen than of nitrogen; so that the air which fishes breathe is richer in oxygen than that which we breathe.

The principal constituents of the atmosphere are water, carbonic anhydride, nitrogen, and oxygen.

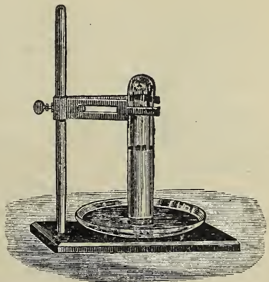

FIG. 2.

3. We must also determine the constituents of water, because it is an efficient agent in producing chemical changes.

Exp. 4.—Fill a stout test tube with water and invert this in a dish of water. Pass into the mouth of the tube a small pellet of

*If the teacher has no mercurial cistern, he may remove the oxygen by phosphorus, or, better, by potassium pyrogallate (see **Exp. 78**).

sodium wrapped in filter paper. Bubbles of gas instantly rise to the top of the tube and force the water out. Remove the tube from the water, and apply a lighted splinter to its mouth. The gas burns with a pale flame.

This gas is called *hydrogen*, and constitutes $\frac{1}{9}$ of the weight of water. Test the water of the dish by reddened litmus paper; it will become blue. Moisten another litmus paper, and put a little of the sodium oxide, obtained by Exp. 3, on it; the same change of color will be produced, because sodium oxide has also been formed by the decomposition of the water.

Water, then, is composed of hydrogen and oxygen. When sodium oxide dissolves in water, it forms sodium hydrate, or the caustic soda of the apothecary (Na_2O, H_2O, or $2NaHO$).

Exp. 5.—Boil a few leaves of red cabbage in water, and decant the clear, purplish liquor. Caustic soda dropped in this infusion changes it to a green color.

Bodies which are capable of changing such vegetable blues to green are called, in ordinary language, *alkalies.* The common alkalies are soda, potassa, and ammonia. They have an acrid taste and a soapy feel.

Exp. 6.—Prepare chlorine water as directed in § **122.** A little of this dropped in the cabbage infusion, or on litmus paper, will instantly decolorize or bleach it.

Exp. 7.—Fill a flask completely with chlorine water, invert it in a cup of water, and expose it for some days to the sunlight. Bubbles of gas will collect in the upper part of the flask, and the odor of the chlorine and its bleaching power will entirely disappear if it is exposed long enough.

Exp. 8.—Light a splinter of pine, and blow out the flame so as to leave only a glowing coal. Plunge this into the gas of the flask: it will instantly be re-lighted, and burn brightly.

This gas supports combustion, and is called *oxygen.* It constitutes $\frac{8}{9}$ of the weight of water. The chlorine has also decomposed the water; but, unlike sodium, it

liberates oxygen and combines with the hydrogen. The compound formed is called hydrogen chloride, or, more frequently, hydrochloric acid (HCl).

Test the water in the cup with the cabbage infusion or with blue litmus paper. It will be reddened,* and the water will have a sour taste.

Bodies which change vegetable blues to red are called, in ordinary language, *acids*. The common acids have a sour taste.

These experiments show that water contains oxygen and hydrogen. The following experiment shows that it contains only these gases.

Exp. 9.—Prepare hydrogen as directed in § **82**; dry it by passing the gas through a tube filled with calcium chloride, and attach to this a delivery tube drawn out to a fine orifice. After all the air has been expelled from the apparatus,† light the hydrogen, and hold over the flame a cold bell glass (Fig. 3). The hydrogen burns because it unites with the oxygen of the air, and the product of the combustion collects in drops on the inside of the bell glass. (See §§ 46 and 47).

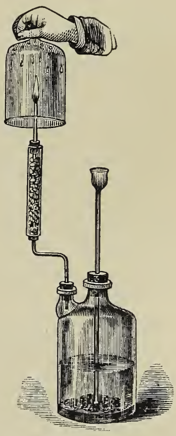

Fig. 3.

It is *water* (H_2O). Two parts, by weight, of hydrogen unite with sixteen parts, by weight, of oxygen to form eighteen parts of water. Thus, eight ounces of oxygen are required to burn one ounce of hydrogen to form nine ounces of water. These last quantities are evidently in the same proportions as those first given; or, 2 : 16 :: 1 : 8.

These proportions are always the same. Because they are constant, and because the constituents can not be separated from each other by merely physical means, we say that water is a true chemical compound.

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* If all the odor of the chlorine has not disappeared, it will also be more or less bleached.

† Hydrogen mixed with air is *dangerously explosive.*

The aqueous vapor in the atmosphere promotes many chemical changes: thus, iron and wood will remain unchanged for years in dry air; but in moist air, the iron readily rusts and the wood decays. The oxygen which causes the oxidizing of metals and the decay of vegetable matter is obtained by the decomposition of water.

4. **Chemistry** treats of the composition of bodies, and of those changes in matter by which the substances acted upon suffer a loss of identity.

The chemist endeavors to determine the composition of bodies by subjecting them to various experiments, which are designed to effect essential changes in their structure. By many such it has been found that a limited number of substances consist of a single uniform kind of matter — as, sodium, oxygen, hydrogen; and that by far the greater number of substances are composed of two or more constituents — as, water, sodium oxide, sodium hydrate.

5. Bodies which have been made to yield but one kind of matter are called *simple substances* or *elements*.

Bodies which may be separated into two or more elements are called *compound substances*.

The known elements are sixty-five in number. There can be no doubt that others will be discovered; and it is possible that some substances which are now considered simple will hereafter be found to be compound.

TABLE OF THE ELEMENTS.

I. The Non-Metals — 13.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Fluorine	F	19.	Boron	B	11.
Chlorine	Cl	35.5			
Bromine	Br	80.	Carbon	C	12.
Iodine	I	127.	Silicon	Si	28.
Oxygen	O	16.	Nitrogen	N	14.
Sulphur	S	32.	Phosphorus	P	31.
Selenium	Se	79.4			
Tellurium	Te	128.			

II. The Semi-Metals — 13.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Vanadium	V	51.3	Titanium	Ti	50.
Arsenic	As	75.	Zirconium	Zr	89.6
Niobium	Nb or Cb	94.	Tin	Sn	118.
Antimony	Sb	122.			
Tantalum	Ta	182.	Molybdenum	Mo	92.
Bismuth	Bi	210.	Tungsten	W	184.
			Uranium	U	120.

Hydrogen —— H 1.

III. The Metals — 39.

Lithium	Li	7.	Cerium	Ce	92.
Sodium	Na	23.	Lanthanum	La	92.8
Potassium	K	39.1			
Rubidium	Rb	85.4	Thallium	Tl	203.6
Caesium	Cs	133.	Lead	Pb	207.
			Thorium	Th	231.
Silver	Ag	108.			
			Chromium	Cr	52.4
Glucinum	Gl or Be	9.4	Manganese	Mn	55.
Magnesium	Mg	24.	Iron	Fe	56.
Zinc	Zn	65.	Cobalt	Co	59.
Cadmium	Cd	112.	Nickel	Ni	59.
Calcium	Ca	40.	Gold	Au	197.
Strontium	Sr	87.5			
Barium	Ba	137.	Ruthenium	Ru	104.4
			Osmium	Os	199.2
Copper	Cu	63.5			
Mercury	Hg	200.	Palladium	Pd	106.6
			Platinum	Pt	197.4
Aluminium	Al	27.5	Rhodium	Rh	104.4
Gallium	Ga	69.9	Iridium	Ir	198.
Indium	In	113.4			
Yttrium	Y	61.7	Davyum	Da	150?
Didymium	Di	96.			
Erbium	Er	112.6			

NOTE.—The atomic weights are those given in the "Neues Handwoerterbuch der Chemie." Other classifications are given on pp. 59, 60, 192.

The symbol placed after each element is the abbreviation of its Latin name; thus, H stands for hydrogen; Ag for silver (Argentum); Hg for mercury (Hydrargyrum); Fe for iron (Ferrum). These symbols are so convenient that the student should at once familiarize himself with those of the most common, the names of which in the table are printed in capitals.

6. **The study of Chemistry** is much facilitated by classifying the elements in groups, whose members have many characteristics in common. But it is impossible to draw any strict dividing line; and hence all such groupings must be regarded as made merely for the sake of convenience, and liable to be varied hereafter. It will be noticed that three principal groups are given: the non-metals, the semi-metals, and the metals. No definition has been given which sharply distinguishes them; but it may be generally observed, (1) That the metals are good conductors of heat and of electricity, and are characterized by a peculiar metallic luster; (2) The non-metals are non-conductors of heat and of electricity; (3) The metals are electro-positive elements, and the non-metals electro-negative. By this we mean that when their compounds are decomposed by the galvanic current, the metals tend to collect at the negative pole of the battery, and the non-metals at the electro-positive pole.* (4) Generally, the non-metals form, with oxygen, acid anhydrides, while the metals form basic anhydrides, as will be explained hereafter. (5) The semi-metals are elements which resemble the metals in their physical properties, and the non-metals in their chemical properties; that is, they have the luster of the metals, but their oxides are most frequently acid anhydrides.

7. **The most important processes employed** in chemistry are readily illustrated by a few experiments, which the student is earnestly requested to repeat for himself.

*See § 48.

I.—Combination.

Exp. 10.—Cut off a thin slice of phosphorus, and, having dried it between two folds of filter paper, lay it on a dry plate. Now put upon this a flake of iodine. The two elements unite and evolve so much heat that a portion of the phosphorus combines also with the oxygen of the air, and burns brightly. White fumes are given off, which are a compound of phosphorus and oxygen, called phosphorus pentoxide. The red solid that remains on the plate is called phosphorus iodide.

Exp. 11.—Rub together in a mortar a small globule of mercury with a little more than five-fourths of its weight of iodine, moistened with a few drops of alcohol. The mercury and iodine unite to form a scarlet powder, which is called mercuric iodide.

Exp. 12.—Place a bright strip of zinc in a small dish, and cover it with water. Now drop on the zinc a few flakes of iodine. After a few hours the iodine will disappear in the liquid. It has united with a portion of the zinc to form zinc iodide. The combination may be accelerated by frequent stirring, and by gently warming the mixture.

If, now, the remaining zinc be removed, the zinc iodide may be obtained by evaporating the liquid on a water bath.

Exp. 13.—Prepare a strong solution of chlorine water, as directed in § **122.** Put some of this in a glass vial, with a very small globule of mercury, and shake frequently. After a time the mercury will disappear, and most of the odor of the chlorine; the chlorine will unite with the mercury to form mercuric chloride.

This body may be obtained by evaporating the liquid, or the solution may be used in the experiments which follow.

8. These experiments show that two bodies may combine directly.

The process of uniting two bodies to form a chemical compound is called *synthesis*. When only two elements enter into combination, the product is called a *binary* compound. Such compounds are named by affixing the termination *ide* to the non-metallic, or electro-negative, element, and prefixing the name of the metal, or the electro-positive element; as, zinc iodide, mercuric iodide.

In this way we may name the oxides, chlorides, iodides, phosphides, etc.; but it is important to note that the termination *ide* is never used except with binary compounds.

9. The foregoing experiments show that chemical changes are marked by alterations in color, taste, odor, form, and sometimes by the development of heat and light. The compounds formed are essentially different from the elements that enter into combination. On the other hand, if bodies are merely mixed together, no such changes occur.

Exp. 14.—Rub together in a mortar 56 parts of iron filings and 32 of sulphur. Divide the mixture into four equal portions. From the first portion the iron may be removed by a magnet; from the second portion the sulphur may be removed by dissolving it in carbonic disulphide; and from the third, by directing upon it a gentle stream of water, which will suffice to wash away the lighter particles of the sulphur, and leave the heavier iron behind. Now heat the fourth portion in a test tube. The sulphur and iron combine to form ferrous sulphide, which is a true chemical compound whose constituents are inseparable by mechanical means.

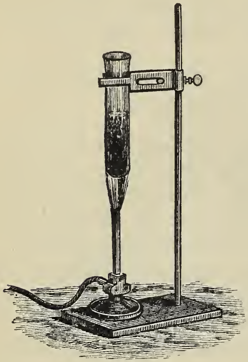

FIG. 4.

Further, a mixture may be made in all conceivable proportions. This is not the case in a chemical combination. In Exp. 12, a portion of the zinc was not acted upon. If in Exp. 11 we employ too much iodine, the excess will remain uncombined and mixed with the mercuric iodide. In the last example, if an excess of sulphur is used, it may be dissolved by carbonic disulphide, after first pulverizing the product.

10. Law of constant proportions.—*In every chemical compound, the proportions of the elements united are always fixed, definite, and invariable.*

Thus the following named binary compounds are always found to contain:

Sodium chloride,	23	parts of	sodium,	35.5	parts of	chlorine.
Sodium iodide,	23	"	sodium,	127	"	iodine.
Potassium chloride,	39	"	potassium,	35.5	"	chlorine.
Potassium iodide,	39	"	potassium,	127	"	iodine.
Zinc iodide,	65	"	zinc,	254	"	iodine.
Zinc chloride,	65	"	zinc,	71	"	chlorine.

These are the only binary compounds of iodine and chlorine with sodium, potassium, and zinc. Iodine and chlorine, however, combine with some of the elements to form two or more distinct compounds; but for the same compound, the proportions are always constant.

Exp. 15.—Repeat Exp. 11, using only five-eighths as much iodine as mercury. A greenish-yellow powder will be produced, containing twice the proportional quantity of mercury. It is called mercurous iodide (HgI, or Hg_2I_2).

If a quantity of iodine intermediate between five-fourths and five-eighths its weight of mercury be used, both iodides will be produced and remain mixed together. Strong alcohol will dissolve out of the mixture the mercuric iodide, and leave the mercurous iodide behind.

Mercury, therefore, forms two compounds with iodine: 200 parts of mercury may combine with 127 parts of iodine to form mercurous iodide, or with 254 parts of iodine to form mercuric iodide. The proportion of iodine in the second is exactly twice that of the first. We distinguish between two such compounds by the terminations *ic* and *ous* added to the more positive element: the *ic* denoting the higher degree of combination; the *ous*, the lower.

Exp. 16.—Boil a solution of mercuric chloride with a globule of metallic mercury. A white powder will separate from the mixture. This is mercurous chloride ($HgCl$, or Hg_2Cl_2).

The proportion of chlorine in the mercuric chloride is twice that in the mercurous chloride. Some such simple relation is generally found when two elements form more than one compound. Hence:

11. The Law of multiple proportions.—*When one body is capable of uniting with another body in several proportions, these proportions bear a simple relation to each other.*

Thus, an element, A, may unite with another element, B, to form compounds, which may be represented by

$$A + B,\ \ A + 2B,\ \ A + 3B,\ \ A + 4B,\ \ A + 5B,$$
$$2A + 3B,\ \ 2A + 5B,\ \ 2A + 7B, \text{ etc., etc.}$$

We have an excellent illustration of this law in the compounds of nitrogen and oxygen. These are five in number:

	PARTS IN 100 BY WEIGHT.		RATIOS.		
	N.	O.	N.	O.	SYMBOLS.
Nitrous oxide,	63.64 :	36.36 ::	28 :	16	N_2O
Nitric oxide,	46.67 :	53.33 ::	28 :	32	N_2O_2
Nitrous anhydride,	36.85 :	63.15 ::	28 :	48	N_2O_3
Nitric peroxide,	30.44 :	69.56 ::	28 :	64	N_2O_4
Nitric anhydride,	25.93 :	74.07 ::	28 :	80	N_2O_5

This shows that 28 parts of nitrogen may combine to form a series of compounds with oxygen, containing one, two, three, four, and five times 16 parts of oxygen. When a series of binary compounds is formed of two elements, we may distinguish between them by the prefixes *mono* or *prot* = one; *bi*, *deut*, or *di* = two; *tri* or *ter* = three; *sesqui* = two to three; *tetra* = four; *penta*, five, etc., affixed to the element that increases by multiples. Sometimes, also, the names of the elements are separated by *of*: thus the last series may be severally named protoxide, dioxide, trioxide, tetroxide, and pentoxide of nitrogen.

Many compounds have two or more names: one the vulgar name, others derived from former theories of chemists, and still others in modern use. Thus the two chlorides of mercury have each a half a dozen names. the following of which are still allowable:

Formula,	Hg_2Cl_2, or HgCl.	$HgCl_2$.
Vulgar name,	Calomel.	Corrosive Sublimate.
Old name,	Protochloride of Mercury.	Bichloride of Mercury.
New name,	Mercurous Chloride.	Mercuric Chloride.

12. It follows naturally, from the laws of constant and multiple proportions, that the weights in which bodies unite may be represented by numbers. We also find that the same number, or a multiple of it, will represent the proportion, by weight, in which any element will combine with any other element. Thus iodine may always be represented by 127, or by some multiple of it. The numbers thus found are called the *combining numbers* of the elements.

Law of combining proportions.—*Every element in combining with other elements does so in a fixed proportion, which may be represented numerically.*

The numbers given on pp. 12 and 13 are the combining proportions in which each element unites with the other elements. Further, it has been agreed that each symbol shall not only be an abbreviation of the name of an element, but also represent one combining number. Hg, therefore, represents 200 parts of mercury by weight; I, 127 parts of iodine; O, 16 parts of oxygen, etc. A number placed below a symbol represents how many multiples of the element are taken: thus, I_2 represents two combining proportions, or 254 parts, of iodine. We may then represent mercurous iodide by HgI, or by Hg_2I_2, and mercuric iodide by HgI_2. If we desire to represent a multiple of a compound, we do so by placing a numeral before the symbol of the compound; thus,

$2Hg_2I_2$ represents two proportions of mercurous iodide; $2HgI_2$, two proportions of mercuric iodide. The number, when placed before a compound, multiplies each element in the compound by itself. The same thing is sometimes done more conveniently by inclosing the symbols within parentheses, and placing the numeral either before or below the parenthetical marks; for example, $2HgI_2$, $2(HgI_2)$, $(HgI_2)_2$, represent the same quantities.

13. Binary compounds may also unite and produce other compounds.

Exp. 17.—Quicklime (CaO) and water (H_2O) are binary compounds. Put a large lump of quicklime on a plate, and pour on it a small quantity of water. The two binaries unite; the lime becomes heated and crumbles away to a light powder, which is called slaked lime. Its composition may be represented by CaO, H_2O, or CaH_2O_2, or $Ca(OH)_2$.

Exp. 18.—Place a piece of clean sodium in a bottle filled with dry air or oxygen. The sodium changes to sodium oxide (Na_2O). Now bring into the flask a stream of carbonic anhydride (CO_2).* The two binary compounds unite to form sodium carbonate (Na_2O, CO_2, or Na_2CO_3).

When two binary compounds unite, the product contains three elements, and is called a *ternary* compound. Thus, sodium carbonate contains three elements, Na, C, and O.

A few compounds are formed by the union of two ternaries. These usually contain four elements, and are called *double salts.* Common alum is an example: it consists of potassium sulphate and aluminium sulphate; besides which it contains water, which is called water of crystallization. The entire formula of alum is K_2O, $SO_3 + Al_2O_3$, $3\,SO_3 + 24H_2O$, or $K\,Al\,2\,SO_4 + 12\,H_2O$.

14. Compounds may also be formed indirectly.

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* The directions for the preparation of this are on page 171.

II.—Substitution.

Exp. 19.—Put a little mercuric iodide in a vial half filled with water. Add a few drops of saturated chlorine water, and shake the mixture. A part of the iodine is set free and darkens the liquid. The mercury is not seen, because it has combined with the chlorine to form mercuric chloride, and is dissolved. The odor of the chlorine also disappears.

The whole of the iodine may be displaced by the chlorine, by adding the chlorine water in small quantities, and shaking the mixture after each addition. The free iodine may be separated from the mixture by adding a teaspoonful of chloroform to the water, and shaking. The chloroform dissolves the iodine and settles to the bottom. The supernatant liquid may then be poured off, and the mercuric chloride be obtained by evaporation.

Exp. 20.—Mercurous iodide, treated in the same way, yields mercurous chloride and free iodine.

Exp. 21.—Put another portion of mercuric iodide in a small beaker with a little water. Place in this a clean zinc strip, and warm gently. In a few hours the mercuric iodide will entirely disappear, and a coating of mercury will be seen on the zinc. In this case the zinc has displaced the mercury in the compound, and has formed zinc iodide, which remains in the solution. It may also be obtained by filtering and evaporating the liquid.

15. These experiments show that we may form new compounds by displacing one element by another. The process of forming a new compound by displacement is called *substitution.*

III.—Metathesis.

Exp. 22.—Pour into a test tube a solution of mercuric chloride, and add to this, drop by drop, a solution of zinc iodide. The elements of the two compounds will be rearranged to form two new compounds,—solid, red, mercuric iodide and zinc chloride.*

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*The student will notice that the red powder, which is at first formed, immediately disappears, because an *excess* of mercuric chloride dissolves it: that it then settles to the bottom of the tube, or *precipitates;* and, finally, if more zinc iodide is added, and the mixture shaken, it again disappears, because an *excess* of zinc iodide dissolves it. The example shows the importance of avoiding excess in chemical manipulations. A drop too much is *excess.*

If the mercuric iodide be filtered off, the zinc chloride, which remains dissolved, may be obtained by evaporating the solution to dryness.

Exp. 23.—Provide a small flask, as shown in Fig. 5, with a cork through which passes a long funnel tube, A, reaching nearly to the bottom of the flask; also a shorter tube, B, bent at right angles, and just passing through the cork. Make all the fittings air-tight. Now put some ferrous sulphide in the flask, and insert the cork. Pour through the funnel tube a little hydrochloric acid. Chemical action will immediately begin, and an extremely offensive gas, hydrogen sulphide, will be given off.

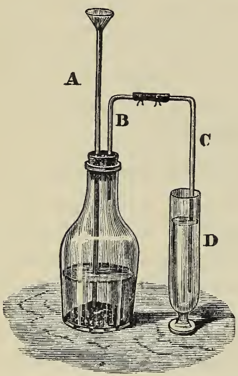

Fig. 5.

Hydrochloric acid is a solution of hydrogen chloride. When this is poured on ferrous sulphide, the elements are arranged into two new compounds, — ferrous chloride and hydrogen sulphide.

Exp. 24.—Having previously attached, by a rubber tube, the glass tube, C, to the flask, pass the escaping hydrogen sulphide into any of the compounds of mercury previously obtained. They will all blacken from the formation of mercurous sulphide, or mercuric sulphide, and the hydrogen will enter into combination with the iodine or with the chlorine.

16. These experiments show that new compounds may be formed by an interchange of the elements previously existing in other compounds.

The process of forming new bodies by an interchange of the elements of two compounds is called *double decomposition*, or *metathesis*.

17. Chemical changes like those already described are called *reactions;* the bodies which take part in them are called *reagents*. We may represent reactions by equations not unlike those of algebra. The sign + represents

added to, or *and;* the sign —, *taken from;* the sign =, *produces*, or *results in.* Thus, the formula,

$$\mathrm{Hg\,Cl_2 + Zn\,I_2 = Hg\,I_2 + Zn\,Cl_2}$$

means "zinc iodide *added to* mercuric chloride, *produces* mercuric iodide and zinc chloride." The formula is never correct unless the sum of the combining numbers on one side of the sign of equality is exactly equal to the sum on the other.

$$\begin{array}{ccccccc} \mathrm{Hg\,Cl_2} & + & \mathrm{Zn\,I_2} & = & \mathrm{Hg\,I_2} & + & \mathrm{Zn\,Cl_2} \\ \underbrace{200+71}_{271} & + & \underbrace{65+254}_{319} & = & \underbrace{200+254}_{454} & + & \underbrace{65+71}_{136} = 590 \end{array}$$

Further, if we have given the left-hand side of the equation, and one product, we can predict, in many cases, what the other product will be. It will generally be a combination of the elements not used to form the product given.

In this book, the sign $\frown$ placed over a symbol indicates that a gas is evolved; the sign $\smile$ placed beneath, that a solid is formed and precipitates.

Having by some one of these methods obtained a new compound, the chemist endeavors to confirm the conclusions he has reached respecting the composition of the body, by again separating it into its elements.

IV.—Analysis.

18. The process of separating a compound into its constituents is called *analysis.*

Exp. 25.—Place a gramme of mercuric oxide in a tube of hard glass, and heat strongly. It will be decomposed into mercury and oxygen. The former will collect in metallic globules on the colder portions of the tube, and the latter will escape as a gas. The presence of oxygen in the tube may be tested by first lighting a splinter of pine, then blowing it out so as to leave a glowing coal.

and introducing this into the tube. If oxygen is present, the coal will burst into a flame. The oxygen may be collected by previously connecting to the glass tube, by means of a perforated cork, a delivery tube which dips under water in a pneumatic cistern, as in Fig. 6. A cylinder filled with water is then inverted over the mouth of the delivery tube. As fast as the gas is evolved, it rises into the cylinder, and is there collected.

Every 216 parts, by weight, of the red oxide yields 200 parts of mercury and 16 of oxygen, also by weight.

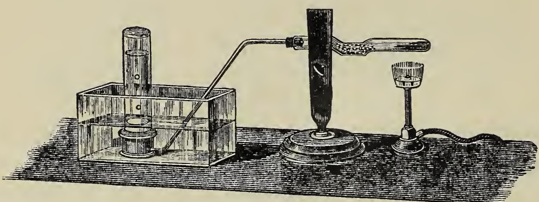

FIG. 6.

Exp. 26.—Heat iodic anhydride in apparatus similar to that shown in Fig. 6. It separates into oxygen and iodine. The iodine at first fills the tube with a purple vapor, which soon condenses in grayish-black flakes. The oxygen may be collected and examined as before.

Every 334 parts, by weight, of iodic acid yields 254 parts of iodine and 80 of oxygen.

Exp. 27.—Heat dry mercuric iodide in a dry test tube. It does not decompose, but is changed to vapor, which condenses in yellow crystals near the top of the tube. This is called *sublimation.* If some of these yellow crystals are shaken out upon paper and rubbed with a knife-blade, they become red; heated again upon the paper, they become yellow; again rubbed, red; and so on. No chemical change, however, has taken place.

19. **Mere change of temperature** will not suffice for the analysis of this body. We may, however, determine its composition indirectly. Thus, by making such weighings as are necessary, we may ascertain, in Exp. 19,

that every 454 parts of mercuric iodide yields 254 parts of iodine; by Exp. 21, that the same quantity yields 200 parts of mercury. Also, by Exp. 22, that to form 454 parts of mercuric iodide requires 271 parts of mercuric chloride and 319 parts of zinc iodide; and, by similar experiments, learn that 271 parts of mercuric chloride contain exactly 200 parts of mercury, and that 319 parts of zinc iodide contain exactly 254 parts of iodine. Finally, we may determine, by Exp. 11, that the exact proportions required to form mercuric iodide are 200 parts of mercury and 254 parts of iodine. Since all these agree, we are certain that the result is correct.

20. When reagents are employed to determine *what* elements are present in a body, the process is called *qualitative analysis.* When reagents are employed to determine *how much* of an element is present in a body, the process is called *quantitative analysis.*

21. We have learned by these experiments that different substances combine *with different degrees of energy.* Phosphorus and iodine unite as soon as they are brought in contact. Mercury and iodine require to be triturated, or rubbed together; but, once united, the compound is not decomposed by heat. On the other hand, the red oxide of mercury may be formed by prolonged heating of mercury in the air, at a temperature of about 315° C., and is again decomposed into its constituents at a dull red heat.

We have also learned that the same matter may successively form a part of several different compounds. With sufficient care in experimenting, we can follow the same matter through a dozen changes without losing a particle. *No matter is destroyed* by chemical changes, however many they are, or however violent they may appear.

Recapitulation.

All substances are either simple or compound, or are mixtures.

Simple substances are . . . { electro-negative { non-metals, 13. / semi-metals, 13. } / electro-positive — metals, 39. }

Compound substances contain { two elements — binary. / three elements — ternary. / four elements — double salts. }

In binary compounds —
The negative element takes the termination *ide.*
It may take the prefix *mono, di, tri, tetra,* or *penta.*
The positive element may take the termination *ous* or *ic.*

Chemical changes are produced —
By the union of two bodies . . . . Combination.
By displacing one element by another . . . . Substitution.
By an interchange of elements . . . . Metathesis.
By the decomposition of bodies . . . . Analysis.

Analysis is either Qualitative or Quantitative.

The laws of combination are —
The law of constant proportions.
The law of multiple proportions.
The law of combining proportions.

CHAPTER II.

CHARACTERISTICS OF CHEMICAL AFFINITY.

22. Few of the elements exist, as such, free in nature. Gold, platinum, copper, mercury, silver, sulphur, and carbon are found native, but most of the others have been obtained only from their compounds. The unstratified portion of the earth's crust, which is considered to be the source from which the other rocks are formed, consists mainly of the compounds of eight elements, although it contains traces of many others.

The principal constituents of the primary rocks are given in the following table, together with the weights of each, reckoned on a scale of 100 parts.

Oxygen, 46.	Aluminium, 8.	Calcium, 3.5.	Potassium, 2.4.
Silicon, 30.	Iron, 6.	Sodium, 2.5.	Magnesium, 1.4.

We find in the stratified rocks minerals containing comparatively large quantities of carbon, sulphur, arsenic, and chlorine. The metals — copper, lead, zinc, and tin — are somewhat abundant, although their ores are sparsely distributed in mineral veins.

23. The waters of the earth are composed of hydrogen and oxygen, but contain in solution notable quantities of sodium chloride and other salts.

The atmosphere is a mixture of nitrogen, oxygen, and small amounts of carbonic anhydride and aqueous vapor.

Small quantities of phosphorus are found in plants and animals.

The nineteen elements named are the only ones which are found in great abundance. The greater portion of the remaining elements are seldom met with, and some of these are so rare that they have been handled by but few chemists.

24. The force which holds like particles of matter together is called *cohesion.* It is strongly exerted in solids, feebly in liquids, and appears to be entirely absent in gases. The energy of cohesion is dependent: (1) on the kind of matter; thus, it is evident that the particles of iron cohere with greater energy than those of lead, because it requires a greater force to pull them apart: (2) on the temperature; water, a liquid at ordinary temperatures, changes in the cold of winter to solid ice, and, on boiling, passes away in aëriform steam: (3) fluids are greatly influenced by pressure; thus, if ether, a liquid, under the pressure of one atmosphere, be introduced into

the vacuum at the top of a barometer tube, it instantly changes to vapor. (See Norton's Nat. Philos., Art. 569). The cohesion of any substance is, therefore, only relative.

25. Fifty-eight elements are, at ordinary temperatures, solids; but even refractory solids, like copper, silver, and gold, have been melted and volatilized. Mercury and bromine, the only elements which are ordinarily liquid, easily vaporize and are as easily solidified by comparatively slight changes in temperature. Under the joint influence of cold and pressure, chlorine, a gaseous element, becomes liquid; and some compound gases, like ammonia and carbonic anhydride, become not only liquid, but solid.

Gases like these are called *coercible gases.** The resources of experiment have lately availed to condense oxygen, nitrogen, and hydrogen. These elements, however, from the difficulty experienced in condensing them, are frequently spoken of as the *permanent gases.* It is probable that any one of the elements may be obtained in either the solid, liquid, or aëriform condition. This statement is also true of many compounds; but a large

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* The following gases are condensed to liquids at a temperature of 0° C., under the atmospheric pressures named below:

		PRESSURE IN ATMOSPHERES.			PRESSURE IN ATMOSPHERES.
Sulphurous anhydride,	SO_2	1.53	Sulphuretted hydrogen,	H_2S	10.
Cyanogen,	CN	2.37	Hydrochloric acid gas,	HCl	26.20
Ammonia,	NH_3	4.40	Nitrous oxide,	N_2O	32.20
Chlorine,	Cl	6.	Carbonic anhydride,	CO_2	38.50

The following bodies have been condensed to liquids under a pressure of one atmosphere, at the temperatures given below:

Carbonic anhydride,	— 78° C.	Bromine,	+ 63° C.
Chlorine,	— 35°	Water,	+ 100°
Cyanogen,	— 21°	Iodine,	+ 200°
Sulphurous anhydride,	— 10°	Mercury,	+ 350°

In condensing gases it is usual to employ conjointly, when possible, the effect of cold and of pressure. O is condensed at —140° under a pressure of 320 atmospheres; N, at + 13°, and under 200 atmospheres. When H was allowed to expand suddenly from a pressure of 280 atmospheres, it apparently formed solid particles described as "hail." The cold produced by the sudden expansion must have been very great.

number of these bodies, of which marble and wood are examples, are so readily decomposed by heat, that we can not hope to volatilize them.

It is well to remark that in chemistry no distinction is drawn between gases and vapors.

26. The force which unites unlike particles of matter, and keeps them in combination, is called *affinity*. It acts between different substances with a different amount of energy, and is modified by the other molecular forces. Although most of the experiments in this book illustrate the characteristics of chemical affinity, the following examples are given to familiarize the student with some of the most important.

27. Affinity varies with the kind of matter. Iodine readily unites with the metals, but all metallic iodides are decomposed by free chlorine, showing that the affinity of chlorine for metals is stronger than that of iodine. Nevertheless, iodine has a stronger affinity for oxygen than chlorine has.

Exp. 28.—Add weak chlorine water to a solution of potassium iodide, to which some boiled starch has been added. The blue color which is produced shows the presence of free iodine.*

28. It is influenced by the mass or the excess of one substance. Sulphuric acid has generally a stronger affinity for metallic oxides than hydrochloric acid; but if to a solution of blue sulphate of copper a large amount of hydrochloric acid be added, the solution will change to a green color. This shows that cupric chloride has been formed, although, at the same time, sulphuric acid must have been set free. The result must be attributed to the excess in quantity of the hydrochloric acid.

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* $KI + Cl = KCl + I.$

Exp. 29.—Fill a hard glass tube with iron turnings; place this in a furnace and heat to redness. (Fig. 7). Now pass through the tube a current of steam. The water will be decomposed; its oxygen unites with the iron to form an oxide of iron; hydrogen is liberated, and may be collected at the other end of the tube.*

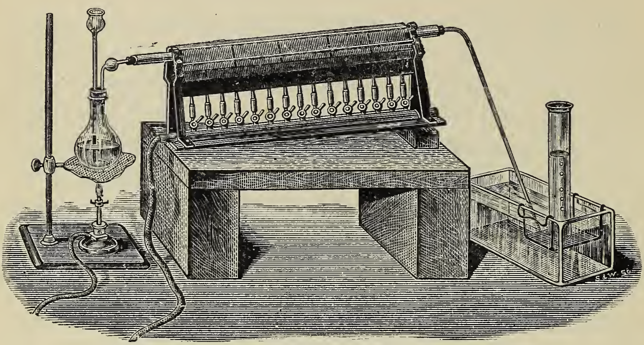

FIG. 7.

Exp. 30.—When the iron is well oxidized, replace the steam by a current of dry hydrogen: the operation is reversed. The oxide of iron is reduced to metallic iron, and steam passes out of the other end of the tube, or collects as drops of water in the colder portions.†

In the first instance, the iron is enveloped by steam, and the hydrogen is at once removed from the sphere of action. In the second instance, the hydrogen is in greater quantity, and the steam formed is prevented from acting upon the iron.

29. The same element does not exhibit the same energy under all circumstances. Thus, if hydrogen be passed into water which contains iodine in suspension, no action will take place. Neither does iodine decompose water to unite with its hydrogen. If, however, iodine is placed in water, together with some other substance that is ca-

*$4\ H_2O + 3\ Fe = Fe_3O_4 + 4\ H_2$. †$4\ H_2 + Fe_3O_4 = 4\ H_2O + 3\ Fe$.

pable of uniting with the oxygen of the water, it readily unites with the hydrogen that is liberated.

Exp. 31.—Add a few flakes of iodine to a solution of potassium iodide. They will dissolve, on stirring, to form a blood-red liquid. Now add this, drop by drop, to a *very dilute* solution of sulphurous acid or of sodium hyposulphite, previously mixed with a very little boiled starch. The sulphurous acid changes to sulphuric acid by uniting with the oxygen of the water.* Hydrogen is liberated, and, at the same instant, unites with the iodine to form hydriodic acid.† So long as this reaction continues, the liquid remains colorless; but as soon as all the sulphurous acid is consumed, the starch will form a blue color with the free iodine.

In this experiment the hydrogen is said to be in the *nascent* state; that is, in the state of being liberated. All bodies in this state have much stronger affinities than when they are used in an isolated form.

Affinity is also influenced by the state of division of matter.

Exp. 32.—Dissolve a few small pieces of phosphorus in carbonic disulphide. Dip a feather into this solution and then draw it quickly over dry paper. The carbonic disulphide soon evaporates and leaves the phosphorus in a finely divided state on the paper. This exposes so much surface to the action of the air, that the phosphorus and oxygen combine rapidly and burst into a flame.

Exp. 33.—Put some alcohol in a saucer and set it on fire. Gunpowder may be dropped through the flame without igniting. If, however, fine iron filings be dropped into the flame, they will burn with bright scintillations. (See **Exp. 194**).

30. Affinity, like cohesion and adhesion, increases with the extent of surface exposed to its action, and is, therefore, generally the more energetic the more finely pulverized the bodies are which are acted upon. An apparent exception to this is found in the fact that a heap

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* $H_2O + H_2SO_3 = H_2SO_4 + H_2$.

† $H_2 + I_2 = 2HI$; or together, $H_2O + H_2SO_3 + I_2 = H_2SO_4 + 2HI$.

of charcoal dust will burn less readily than one of lump charcoal. This is easily explained; for the lump charcoal permits the air to circulate freely between its interstices, and thereby exposes a larger surface than the charcoal dust, which can be enkindled only on the outside of the heap.

31. Affinity varies with the state of cohesion. Chemical affinity acts only at insensible distances. The more points of contact, the more readily will bodies unite. Any thing that tends to overcome the cohesion of a body tends also to augment its affinity for other bodies. Generally speaking, two solids can not be made to unite by pulverizing them together; the principal exceptions being those cases in which a liquid is set free by the reaction.

Exp. 34.—Rub together in a mortar crystals of oxalic acid and caustic lime. The two may be made to unite, because, at the beginning of the action, a little of the water of crystallization of the acid is set free, and acts as a solvent.

Exp. 34. (*a*)—Rub together 5 parts of KI and 4 parts of $HgCl_2$. They will combine to form red HgI_2 and KCl. This is a marked exception.

Exp. 35.—Rub together oxalic acid and sodium carbonate. No apparent action takes place; but, if a little water be added, the two unite with a rapid evolution of carbonic anhydride.

32. It is a general principle that to produce combination, at least one of the bodies must be in the fluid state. We have seen that the cohesion of solids is overcome by heat liquefying or vaporizing them. It may also be overcome by the adhesion of liquid particles, producing what is termed a *solution.*

Exp. 36.—Pulverize 20 grammes of common alum; place it in a flask, and pour over this 50 grammes of cold water. The whole of the alum will not dissolve, even after repeated stirring. Now heat the flask, and all will dissolve. The solution has a sweet and astringent taste.

Exp. 37.—Set the solution away to cool: small, octahedral crystals are speedily formed (see Fig. 8); and, if the liquid is cooled to the freezing point, nearly all the alum will crystallize out.

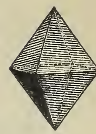

Fig. 8.

Such simple solutions can not be regarded as due to chemical reactions; for, excepting the mere liquefying of the solid, no change has been produced in its properties.

When a solution contains as much solid matter as it is capable of dissolving at any given temperature, it is said to be *saturated.* Common salt is about equally soluble at all temperatures. Some bodies are more soluble at a particular temperature than either above or below it. Thus, the solubility of sodium sulphate increases from 0° C. to 33° C., and then diminishes; but the solubility of most bodies is increased by an elevation of temperature. Marked exceptions are found in some lime compounds.

Exp. 38.—Put a tablespoonful of slaked lime into a pint flask; fill with water, and shake the flask for some time vigorously. Now let it stand undisturbed until the excess of lime has entirely settled to the bottom. Then pour a little of the supernatant fluid into a test tube and heat. It will soon become cloudy, showing that hot water is not as good a solvent for caustic lime as cold water.

33. Simple solutions are generally attended by the absorption of heat, due to the passage of the solid to the liquid condition.

Exp. 39.—Mix two pounds of snow with one pound of common salt. Both will partially dissolve, and a "freezing mixture" will be produced capable of congealing water. A pleasing way of showing this is to select two test tubes of not quite the same size, and, having put a little water in the larger, place the smaller within it. By stirring the mixture with this apparatus, a little cup of ice will be formed between the tubes.

34. There are two kinds of solutions: (1) the *simple solutions*, which have already been described, and (2)

chemical solutions, in which the body first enters into a new chemical compound, which is then dissolved. In chemical solutions, although heat facilitates the formation of the solution, the *quantity* of the body dissolved is always dependent on the quantity of the solvent present; because the proportions in which bodies combine are invariable, and are not affected by differences in temperature. So, also, a chemical solution generally liberates heat.

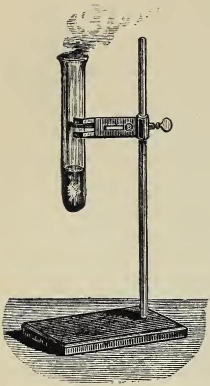

FIG. 9.

Exp. 40.—Place a teaspoonful of copper filings in a test tube, and cover them with strong nitric acid (Fig. 9). Copious red fumes will be given off, the tube will become warm, and, if enough acid be added, all the copper will disappear in the liquid. If this be evaporated, crystals of cupric nitrate may be obtained.*

The liquids used to produce chemical solutions are generally acids. In some cases, aqueous solutions of the alkalies, or of the alkaline sulphides, are employed.

35. The solvents suitable in any given case, either for simple or chemical solutions, are to be learned only in detail. Water is the best solvent for compounds of the metals; alcohol and ether are good solvents for most organic compounds; chloroform and carbonic disulphide dissolve iodine and phosphorus.

The solvent powers of liquids have a wide range. Water dissolves all normal nitrates and chlorates; all chlorides except those of silver, lead, thallium, and the cuprous and mercurous chlorides; and most sulphates—those of barium, strontium, lime, and lead being prominent exceptions. Some bodies, like calcium chloride and

*$3Cu. + 4(H_2O, N_2O_5) + air = 3(CuO, N_2O_5) + 4H_2O + N_2O_4$.

zinc chloride, are so soluble that, if placed in an open vessel, they attract enough water from the air to form a solution. Such bodies are called *deliquescent.*

36. Liquids also dissolve one another: alcohol and water, in all proportions; ether and water, in proportions of about one-tenth of each. Benzene dissolves many oils, and very many of the oils are good solvents for each other.

Solutions of gases are made by passing the gas into cold water or other liquids.* Gases are generally absorbed more abundantly by cold water than by warm water. If a solution of gases be warmed, some of the gas is driven off, and at the boiling temperature, all of the gas is expelled. Boiled or distilled water tastes "flat," because of the absence of the gases usually found in well water. The gases also escape when the solutions which contain them are frozen; that is, when the water becomes solid.

If the temperature remains unchanged, it is also true, within certain limits, that the weight of a gas absorbed by water increases with the pressure. The volume of the gas absorbed remains the same, because the pressure to which it is subjected condenses it.

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* The following table shows how many volumes of the gases named are absorbed by one volume of water and of alcohol, under the pressure of one atmosphere, or at 760 mm. Barometer.

COËFFICIENT OF ABSORPTION.

		WATER.		ALCOHOL.	
		At 0° C.	At 10° C.	At 0° C.	At 10° C.
Hydrogen,	H	0.0193	0.0193	0.02569	0.06786
Nitrogen,	N	0.02035	0.01607	0.12634	0.12276
Oxygen,	O	0.04114	0.03250	0.28397	0.28397
Atmospheric air,		0.0247	0.01953		
Carbonic anhydride,	CO_2	1.7967	1.1847	4.3295	3.5140
Hydrogen sulphide,	H_2S	4.3706	3.5838	17.891	11.9922
Sulphurous anhydride,	SO_2	78.789	56.647	328.62	190.21
Hydrochloric acid,	HCl	500.	418.		
Ammonia,	NH_3	1050.	813.		

Thus, water at 15° C. takes up its own bulk of carbonic anhydride, or about $\frac{1}{500}$ part of its weight. Under pressure of two atmospheres, it absorbs $\frac{1}{250}$ of its weight; of four atmospheres, $\frac{1}{125}$ of its weight, etc. The "soda water" of the confectioner is water charged with carbonic anhydride under pressure. When the pressure is removed, the greater part of the gas escapes with effervescence, because the gas resumes its former volume.

37. When two bodies have a tendency to react upon each other, the affinity between them is greatly modified by the natural cohesion of the product.

Berthollet's first law: *Solutions of two compounds can not be mixed together without a double decomposition taking place, if any two of the constituents can form an insoluble compound.*

We have already had an example that corroborates this, in Exp. 22. Mercuric chloride is soluble, and mercuric iodide is insoluble, in water; hence, if mercuric chloride is mixed with any solution containing a soluble iodide, mercuric iodide will be formed, although we know, by Exp. 19, that the affinity of mercury for free chlorine is stronger than for free iodine.

Exp. 41.—Mix a solution of mercuric chloride with a solution of potassium iodide. Mercuric iodide will be separated. The experiment may be repeated with sodium iodide or zinc iodide.

38. The formation of a solid insoluble in the liquids mixed together is called *precipitation.* The solid which separates is called a *precipitate.*

Exp. 42.—Make an alcoholic solution of potassium acetate, and pass into this a stream of carbonic anhydride: potassium carbonate will precipitate, because it is insoluble in alcohol, and acetic acid will be set free.

Exp. 43.—Add acetic acid to an aqueous solution of potassium carbonate. The reaction will be reversed: viz., potassium acetate will be formed, and carbonic anhydride will be set free as a gas.

We may explain the last reaction thus: (1) the acetic acid has a stronger affinity for potassium than carbonic anhydride; or (2) carbonic anhydride is but slightly soluble in water, and is, besides, naturally an aëriform body.

39. **The volatility of the product** certainly influences affinity. Thus, limestone or calcium carbonate, when strongly heated, breaks up into calcium oxide and carbonic anhydride.

Berthollet's second law: *If any two bodies whose constituents are capable of interchanging and forming a volatile product are heated together, these constituents will unite and volatilize.*

Exp. 44.—Add to a solution of calcium chloride a solution of ammonium carbonate. Calcium carbonate will precipitate, and ammonium chloride remain dissolved in the liquid.*

Exp. 45.—Heat together an intimate mixture of powdered calcium carbonate and ammonium chloride. At a temperature a little above 100° C., calcium chloride and ammonium carbonate will be formed: the latter is volatile and escapes.†

The reaction in Exp. 42 is explained by the first law — an insoluble precipitate is formed: the reaction in Exp. 43, by the second law — a volatile product is formed.

40. **Affinity is in some cases influenced by** *adhesion.*

Exp. 46.—Platinum sponge affords such an extent of surface to the air, that a small piece contains a large quantity of absorbed oxygen. If the dried sponge be brought near a current of dry hydrogen, the two gases are brought so close together that they unite, and the hydrogen is enkindled.

Instances are known of greasy rags, heaped together, taking fire spontaneously within twenty-four hours. The spontaneous combustion of porous bodies like cotton or sawdust saturated with oil is not infrequent, and is due

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* $CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + CaCO_3$.

† $CaCO_3 + 2NH_4Cl = CaCl_2 + (NH_4)_2CO_3$.

to a similar cause. These bodies condense the air within their pores; oxidation commences and liberates a small quantity of heat; this accelerates the oxidation, and thus the process goes on with increasing rapidity until the mass bursts into a flame.

41. Affinity is influenced by heat. This influence may be indirect, as when, in liquefying bodies, the heat is applied to overcome cohesion; but there are many cases in which it acts directly.

Exp. 47.—Endeavor to light the gas from an ordinary burner by a hot iron rod. The gas will not ignite until the iron is at a bright red heat.

The temperature at which bodies enter into combination with the oxygen of the air, so as to produce ignition, varies greatly. No heat is sufficient to ignite iodine, chlorine, or bromine in the air or in oxygen gas. Most of the elements require to be heated before they take fire. Sulphur ignites at about 285° C.; carbonic disulphide vapor is ignited by a warm glass rod, heated to 149° C.; phosphorous is ignited at about 60° C. A match tipped with phosphorous is sufficiently heated by gentle friction to ignite.

Exp. 48.—Place a slip of dried phosphorus on a chip of wood. Fill a test tube with boiling water. Touch the phosphorus with the end of the tube and it will ignite.

A certain temperature is therefore sometimes necessary to induce combination. When the chemical action is once well begun, the heat developed by the union of the bodies is usually sufficient to continue it; but, if this is not the case, or if the heat evolved be too rapidly conducted away, the action ceases.

Exp. 49.—Conduct a stream of dry ammonia gas* into the jet

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* This may be obtained by heating ordinary ammonium hydrate in a small flask, and conducting the vapor through a tube filled with small lumps of quicklime to dry it.

of a Bunsen's burner; it will burn with a pale flame, which is extinguished as soon as the burner is taken away.

If the ammonia is heated by passing it through a hot tube, the flame will be continuous.

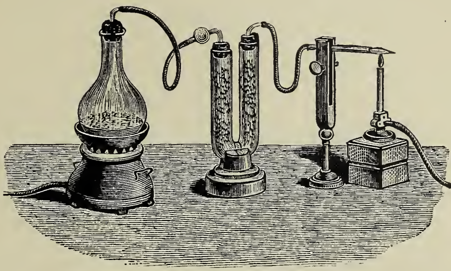


FIG. 10.

Exp. 50.—Bring a cold white plate over an ignited gas jet. Soot will be deposited, because the plate reduces the temperature below that required for the ignition of the carbon present in the flame.

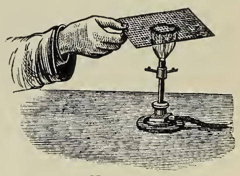


FIG. 11.

Exp. 51.—Bring a sheet of fine wire gauze over an ignited jet of coal gas. The flame is arrested at the under surface of the gauze, because the metal conducts away so much of the heat that the temperature of the gas which passes through the gauze is lower than that necessary to effect combination between the gas and the oxygen of the air. Unignited gas passes through, as may be shown by igniting it above the gauze.

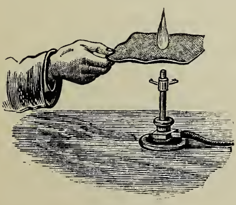


FIG. 12.

Exp. 52.—The gas may be ignited above the gauze without igniting the jet below, as shown in Fig. 12.

42. Heat also effects decomposition. We have already seen, by Exp. 25, that a mercuric oxide is decomposed by heat, although a less heat is sufficient to produce combination of the same elements. So, also, limestone,

or calcium carbonate, is decomposed by strong heat into quicklime and carbonic anhydride, although the affinity between the two is at ordinary temperatures so great that quicklime exposed to the air absorbs the carbonic anhydride contained in it, and again forms calcium carbonate.

Exp. 53.—If a stream of carbonic anhydride is passed over sodium gently heated, it is decomposed with the formation of sodium oxide and carbon (Exp. 172); and a mixture of carbon and sodium oxide, strongly heated, yields again sodium and an oxide of carbon (§353). At ordinary temperatures the affinities of carbon are feeble, but at white heat they are among the strongest known.

43. Chemical combination is usually attended by the evolution of heat, and sometimes also of light. When a substance combines with the oxygen of the air so rapidly as to evolve light, we call the process *combustion*, and say that the substance *burns*. Thus, we say a piece of ignited sulphur *burns;* but when a metal combines slowly with the oxygen and no light is evolved, we say the metal *corrodes*, or *rusts*. Thus, a piece of iron rusts in moist air. In chemical language, both of these processes are examples of combustion; and so, also, true combustion can take place when no oxygen is present.

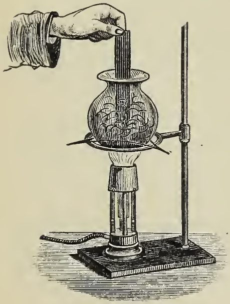


FIG. 13.

Exp. 54.—Strongly heat in a wide-mouthed flask a little sulphur, until the flask is filled with sulphur vapor. Also heat a strip of thin copper foil and plunge it quickly into the sulphur vapor. The two elements combine and evolve heat and light.

It was formerly the custom to classify bodies as *combustible* bodies and *supporters of combustion;* but these terms are manifestly inappropriate; because, when

sulphur burns in air, we should have to call sulphur the combustible body, and, when copper burns in sulphur, the sulphur is the supporter of combustion. Combustion is, in fact, due to chemical combination in which both bodies play an equal or reciprocal part.

Ordinarily, coal gas may be said to burn in air, but air will also burn in an atmosphere of coal gas.

Exp. 55.—Fit a perforated cork to an ordinary lamp chimney, and attach this to a gas burner, as shown in Fig. 14. Fill a gas bag or a large bladder with air, and attach to its mouth a tube drawn out so as to yield a very small jet. Turn on the gas, and after it has escaped for some time, ignite it. Now bring the jet of the bag to the top of the chimney and force out the air. It will ignite, and may then be depressed in the chimney. The air will continue to burn at the jet.

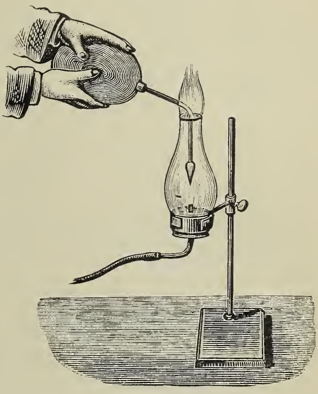


FIG. 14.

In this case, as well as in the ordinary process, the combustion takes place where the two gases meet and enter into combination.

44. The heat of combination varies with the bodies that are brought in combination and the product formed; * but it is important to observe that the same amount of heat will ultimately be evolved, whether the union takes place rapidly or slowly; only, in the latter case, it may not be possible to measure the heat.

The heat of combination may be measured in *thermal units.* A thermal unit is the heat required to raise one pound (or one gramme) of water from 0° C. to 1° C.

* It is probable that the relation between heat and chemical action will soon become an important factor in theoretical chemistry; but, as yet, the results reached are of interest mainly to advanced students.

The following table gives some of the results obtained by burning the substances named in oxygen, chlorine, and iodine vapor.

Heat Developed by Combination

I. With Oxygen.

One pound of	Compound formed.	Thermal units.	One pound of	Compound formed.	Thermal units.
Hydrogen	H_2O	34462	Sulphur	SO_2	2220
Carbon	CO_2	8080	Zinc	ZnO	1330
Phosphorus	P_2O_5	5747	Iron	Fe_3O_4	1582

II. With Chlorine.

Hydrogen	HCl	23783	Zinc	$ZnCl_2$	1529
Phosphorus	P_2Cl_5?	3422?	Iron	Fe_2Cl_6	1745

III. With Iodine.

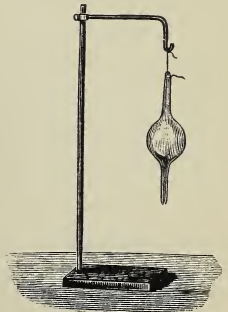
Zinc	ZnI_2	819	Iron	Fe_2I_6	463

The ordinary combustion of wood, coals, and oils are familiar examples of combustion. These bodies are generally compounds of carbon and hydrogen. In burning, they are first decomposed, and then unite with the oxygen of the air to form water and carbonic anhydride.

We may also remark that heat is frequently evolved in the processes of substitution and double decomposition; and sometimes also by direct decomposition, as when gun cotton explodes.*

* In considering these relations of heat, we may have regard to three points: (1) The temperature of ignition; (2) The heat of combination, or the calorific value of a substance; and (3) The temperature attained. This last may be found theoretically, by dividing its available calorific value by the product found by multiplying together the weight of the compound formed and its specific heat. Thus, one pound of hydrogen burning in oxygen evolves 34462 thermal units. The 9 pounds of steam which are formed render latent $537 \times 9 = 4833$ thermal units. The calorific value of the hydrogen remaining will be $34462 - 4833 = 29629$ thermal units, which are available for raising the temperature of 9 pounds of steam. Now, as the specific heat of steam is 0.48, it will require $0.48 \times 9 = 4.32$ thermal units to raise the 9 pounds 1° C. Finally, dividing the available calorific value 29629 by 4.32, we obtain 6930° C., as the temperature to be attained by hydrogen burning in oxygen. It is needless

45. Affinity is sometimes influenced by light. Light plays an important part in the chemical processes of nature, being necessary to the vigorous growth of plants, and contributing not a little to the health of animals. It is not without influence in the operations of a chemical laboratory.



FIG, 15.

Exp. 56.—Fill a clear glass bottle with a mixture of equal parts of chlorine and hydrogen, in a darkened room, and cork the bottle tightly. Wrap it in thick folds of cloth, and, having brought it out into bright sunlight, stand at a distance and pull off the cloth by means of a string previously attached to it. The gases will instantly combine with explosive violence, and shatter the bottle into a thousand fragments.

This experiment succeeds best when the mixture is obtained by the electrolysis of hydrochloric acid. Collect the mixed gases in small bulbs of thin glass, which are easily made from glass tubing. (Fig. 15).

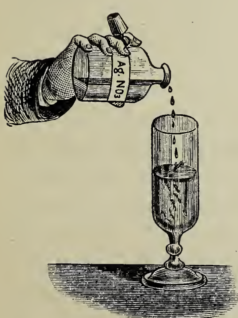


FIG. 16.

In diffused light the action is prolonged, and the union takes place without explosion. In darkness, they do not combine at all.

Exp. 57.—Add a solution of silver nitrate to hydrochloric acid. (Fig. 16.) A white precipitate of silver chloride will be formed. This silver chloride, exposed for a short time to the sunlight, becomes violet, then black. The silver chloride loses part of its chlorine.

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to say that this is never reached, as a large portion of the heat is dissipated. When hydrogen burns in air, the nitrogen has to be warmed, and the temperature attained is about 2740° C. Here also, if the blast of air is too strong, a less temperature will be reached; and it is easily conceivable that a body, by very slow combustion (rotting), may expend nearly all its available heat on surrounding objects.

Light, therefore, acts also as a decomposing agent. The property which light has of darkening silver chloride and silver iodide has been applied in photography.

Exp. 58.—Dip unsized paper in brine made of common salt, and then dry it. By means of a light brush, cover one side of this with a solution of silver nitrate, and dry it in a darkened room. The surface of the paper will be covered with a film of silver chloride. Now oil an ordinary engraving so as to render it translucent. Lay this *closely above* the silvered side of the paper, and expose it to bright sunlight for ten minutes. A reversed, or negative, copy of the picture will be found on the paper. It may be rendered permanent by soaking it for a while in a solution of sodium hyposulphite, to dissolve the silver chloride which has not been changed by the light, and then by washing the paper in water, to remove the hyposulphite. (See **Exp. 125**).

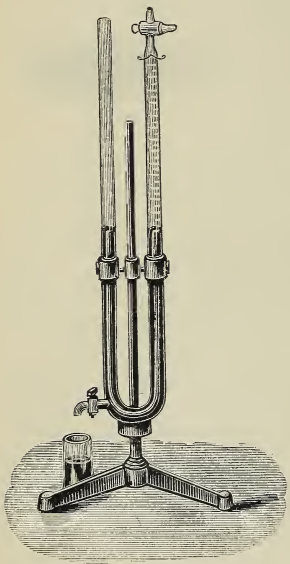

FIG. 17.

On the other hand, light is frequently evolved by chemical combination. This is, in fact, the source of most of our artificial lights.

46. Affinity is influenced by electricity. Frictional electricity will effect the combination of some elements. We may use for this purpose a strong glass tube, called an eudiometer (Fig. 17), open at one end and closed at the other. Through the closed end are melted two platinum wires, whose points are separated so that a spark from a Leyden jar may pass between them.

Exp. 59.—Fill the eudiometer with mercury: then pass into it a measured volume of oxygen and two equal measures of hydrogen, taking care that the mixture does not more than half fill the tube. Close the open end of the tube by a caoutchouc stopper. Now pass an electric spark between the platinum points. A flame will pass down through the gas, showing that combination has taken place. On removing the caoutchouc stopper, the mercury will rise and fill the tube.

If this experiment be modified by inclosing the closed arm of the eudiometer in a larger tube which is kept filled with the vapor of amylic alcohol (a liquid which boils at 132° C.), the water will not condense, but remain as steam. It will then be found, on removing the stopper, that the steam formed by the union of the two gases fills two-thirds of the volume previously occupied by the three volumes of mixed oxygen and hydrogen.

Therefore, when two volumes of hydrogen combine with one volume of oxygen, they condense to two volumes of aqueous vapor.

47. The galvanic current is an energetic agent in producing decomposition of compounds. This mode of decomposition is called *electrolysis*.

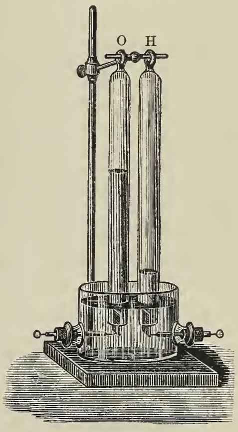

FIG. 18.

Fig. 18 represents an apparatus which may be used to show the decomposition of water. It consists of a glass vessel having two corked openings, through which are passed two wires terminating in platinum electrodes. The vessel being filled with water slightly acidulated with sulphuric acid, two glass tubes, also filled with water, are inverted over the electrodes, and the outer wires are connected with some constant battery. Four Grove's cells are sufficient to cause a rapid decomposition of the water.

Hydrogen rises from the negative electrode, and oxygen from the positive. As water absorbs more oxygen than hydrogen, the gases evolved can not be accurately measured until the water is saturated with the gases. It will then be found that exactly twice as great a volume of hydrogen is evolved as of oxygen. This result confirms Exp. 59.

Other liquids may be decomposed by the same apparatus. Hydrochloric acid evolves hydrogen at the negative and chlorine at the positive electrode. After the liquid is saturated with the gases,—which will require some time if the quantity is considerable,—the two gases are evolved in equal volumes; that is, hydrochloric acid contains one volume of hydrogen and one of chlorine. If both gases are collected in an eudiometer and exploded, it will also be found that they again unite, without condensation, to two volumes.

Fused metallic chlorides yield the metal at the negative and the chlorine at the positive electrode.

If, however, an aqueous solution be used, it may act on one or both of the constituents evolved, and cause a *secondary* action. An aqueous solution of iodide of potassium is easily decomposed; but, as soon as the potassium is liberated, it decomposes the water, forming potassium oxide, and hydrogen gas is liberated at the negative electrode.

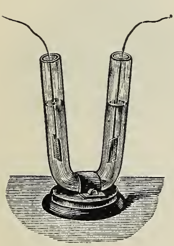

FIG. 19.

Exp. 60.—Fill a U tube with a solution of sodium sulphate, colored by an infusion of red cabbage, and plunge the platinum electrodes in each arm. The fluid at the negative electrode will be colored green, and at the positive electrode, red. We have already learned that these changes in color indicate the presence of an alkali and an acid.

The action is somewhat complex. To explain it we may suppose the sodium sulphate to have the formula, Na_2SO_4. The gal-

vanic action breaks this up into sodium, Na_2, and into SO_4. This last body has never been obtained in a free state, but it is convenient to suppose its existence here. The sodium collects at the negative pole, and the SO_4 at the positive. At both poles a secondary action takes place. A molecule of water is decomposed; its hydrogen unites with the SO_4 to form H_2SO_4, or sulphuric acid; its oxygen, with the sodium to form sodium oxide, Na_2O. This unites with another molecule of water, forming sodium hydrate, Na_2O, H_2O, or $2NaHO$.

48. Since unlike electricities attract each other, the bodies which collect at the negative electrode are called positive, and those which collect at the positive electrode are called negative. These terms are merely relative, as chlorine is electro-positive with reference to oxygen or sulphur, and electro-negative with reference to hydrogen and the metals. The metals and their oxides are generally electro-positive; the non-metals, the semi-metals, and the acid radicals, generally electro-negative.

Exp. 61.—Place in a series of test tubes solutions of the nitrates of (1) lead, (2) copper, (3) mercury, (4) silver. A globule of mercury placed in (4) will reduce the silver, and a nitrate of mercury will be formed. Similarly, a slip of bright copper in (3), of iron in (2), or of zinc in (1), will reduce metallic mercury, copper, or lead, and form the corresponding nitrates, thus exhibiting a difference of affinity which may be referred to the difference in electrical relations. Zinc will reduce most metals from their acid solutions. Sodium amalgam is a still more powerful reducing agent for the metals.

In many such cases of reduction, the water of the solution is first decomposed, its oxygen uniting with the zinc or the sodium, and its *nascent hydrogen* with the acid radical previously combined in the metallic salt. Such reactions are secondary, like those described in Exp. 60.

Generally speaking, the affinities between elements of widely different electricities, as between the metals and oxygen or chlorine, are the strongest; but many stable compounds are known in which both the elements are reckoned as negative; as, SO_2, I_2O_5.

The following is a portion of Berzelius's electro-chemical series, in which any element, counting from oxygen, is electro-negative to those that follow it, and electro-positive with reference to those that precede it.

−	+
Oxygen	Caesium
Sulphur	Potassium
Nitrogen	Sodium
Fluorine	Zinc
Chlorine	Iron
Bromine	Copper
Iodine	Silver
Phosphorus	Mercury
Carbon	Platinum
Antimony	Gold

Hydrogen

±

The galvanic current is maintained by a chemical action which takes place within the cell, proceeding from the plate which is most easily acted upon by the fluid portion of the battery. Not only this, but the quantity of electricity developed is so related to the energy and amount of the chemical action, that the proportions between them can be expressed numerically.

49. There is, therefore, an intimate relation between the force of affinity and the forces of heat, light, and electricity. Affinity may produce heat, light, or electricity. It may be set in action by either of them, and cause bodies to unite, or be so weakened that its compounds are decomposed. Heat may also generate electricity, and electricity be made to evolve heat and light. For these reasons these forces are called the *correlative forces.*

Finally, there are so many cases in which the disappearance of one of these forces is marked by the evolution of another in numerical proportions, that we are

justified in the conclusion that these forces are convertible the one into the other; that affinity, for instance, may reappear as heat, light, or electricity, singly or simultaneously. If this be true, we are not to suppose that when we can no longer trace the action of a force, it has been annihilated, but that it has changed to some other form of force. Force is, therefore, indestructible.

The correlative forces are all thought to be modes of motion impressed upon the ultimate particles of matter in bodies. The difference in the mode of motion determines whether heat, light, electricity, or affinity is produced. Affinity seems to stand in closer relation to electricity than to either of the other forces.

Recapitulation.

The characteristics of chemical affinity:

It varies with the kind of matter;
 with the relative mass of matter;
 is strongest in the nascent state of matter;

It varies with the state of cohesion;
 with the solubility of the product;
 with the volatility of the product.

A fluid state necessary to effect combination.

It is influenced by adhesion;
 by the state of division of matter.

Surface action induces combination.

It is influenced by heat,
 so as to effect combination;
 so as to effect decomposition.

It is influenced by light,
 so as to effect combination;
 so as to effect decomposition.

It is influenced by electricity,
 so as to effect combination;
 so as to effect decomposition.

Correlatively: It may produce heat, light, and electricity.

CHAPTER III.*

CHEMICAL PHILOSOPHY AND NOMENCLATURE.

50. The facts of chemistry are established by experiment, and are capable of being reproduced. They find a practical application in the arts, which is altogether independent of any explanation that may be made of them. When, however, we attempt to reason upon these facts, to classify them, to interpret them, we at once begin to form theories. A theory which renders a reasonable explanation of a great number of facts is useful (1) because it enables us to group them into a system, and (2) because it often leads to new experiments and to the discovery of other facts.

We are liable to three errors: (1) we may assume that to be a fact which has no existence; or (2) we may sometimes mistake a phenomenon, so as to imagine that to be a cause which is only an effect of some unknown cause; or, finally, (3) we may become so accustomed to the language of theory as to mistake its definitions for facts. Once assured of our facts, we may be certain that they are immutable. Nevertheless, it has often happened that statements which have been accepted as facts have been rejected because they have been found to be false; and that one theory has been displaced by another which interprets a greater number of facts.

51. We know nothing of the manner in which the ultimate particles of matter are arranged together: we *believe* that they are arranged in accordance with certain theories which we shall now proceed to develop.

All masses of matter may be subdivided into very small particles; but it is probable that there is a limit

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* To Teachers.—The author advises that young students in chemistry should study, on the advance, only so much of this chapter as is necessary to accept the *fact* of atomicity, and the notation and nomenclature of compounds. The full discussion of chemical philosophy may be deferred until the class has reached Chapter XI. Mature students will find it best to master the subject at this point, where it logically belongs. It is not exceptionally difficult.

to this subdivision, and that all bodies are made up of particles so infinitesimally small that they are inappreciable to our senses. By the terms of this theory,

A molecule is the smallest particle of matter capable of existing in the free state:

An atom is the smallest particle of matter that is capable of entering into or existing in a state of chemical combination.

If we subdivide hydrochloric acid, the least particle that we can obtain, without destroying the identity of the acid, is a *molecule;* but we know that this molecule contains still smaller particles of hydrogen and chlorine. Compound bodies contain the atoms of different elements, united to form *compound molecules;* as, HCl. We suppose, also, that the atoms of the same element may unite to form *elementary* molecules; as, H_2 or Cl_2.

52. It is also believed (1) that the atoms of the same element are exactly alike, and that they have a definite size, shape, and weight; (2) that the atoms of different elements are always unlike, differing in weight and, perhaps, in form; and (3) that equal volumes of all aëriform bodies contain, at the same temperature and pressure, an equal number of molecules.* (4) It also naturally follows that one molecule of any aëriform body must occupy a certain definite space, which is called its *molecular volume*, and that *all molecular volumes are equal.*

Hereafter it will be assumed that all gases are measured when at the temperature of the freezing point of water, and under the pressure of one atmosphere. These are called the *normal* conditions of temperature and pressure.

The following table gives the weight in grammes of 11.2 litres of the following elements, when in the aëriform state, at the normal temperature and pressure:

Hydrogen,	1.	Oxygen,	16.	Phosphorus,	62.
Chlorine,	35.5	Sulphur,	32.	Arsenic,	150.
Bromine,	80.	Selenium,	79.5	Mercury,	100.
Iodine,	127.	Nitrogen,	14.	Cadmium,	56.

* This is known as Avogadro's Law.

These numbers are also the *relative weights* of equal volumes, whether those volumes are measurable or infinitesimal. The student must always remember that a molecular volume or an atomic weight is a definite quantity, although very small.

53. The absolute weight or the volume of any atom is not certainly known.* The combining numbers given on pp. 12 and 13 express the *relative weights* of the atoms, and are called the *atomic weights.* These numbers have been obtained by several extended series of observations. The principal considerations that have led to their adoption are the following:

Hydrogen is the lightest element known. We may therefore take it as the unit by which other substances may be compared; that is, as the standard unit (1) for the specific gravity of gases; (2) for atomic weight; (3) for molecular volume; and, as we shall see hereafter, (4) for the unit of combining power.

We have learned (p. 46) that two volumes of hydrochloric acid gas contain one volume of hydrogen and one of chlorine. Since all molecular volumes are equal, two molecular volumes of hydrochloric acid gas must contain one molecular volume of hydrogen and one

*Physicists have carried the doctrine of molecules further. They find that most of the phenomena exhibited by gases, such as their elastic force, can be satisfactorily explained on the assumption that these bodies consist of perfectly elastic particles, which are perpetually colliding against each other, and against the sides of the vessel which contains them. They have even gone so far as to make an attempt to measure the size and mass of the molecules, the distances between them, and the rate of their motion. The following are Maxwell's results. Two hundred million hydrogen molecules in a row would measure little more than one centimetre. In a cubic centimetre of any gas under the normal conditions of temperature and pressure, there are 19.000,000,000,000,000,000 molecules. The velocity of the hydrogen molecule is 1,843 metres per second. The mass of a molecule of hydrogen is 46 ten-million, million, million millionths of a gramme. The masses of the molecules of all gases are as their atomic weights; hence, the velocity of gases will be inversely proportional to the square roots of their atomic weights. The spaces which separate the molecules are much larger than the molecules themselves. Reckoned in hundred billionths of a metre, a molecule of hydrogen would have a diameter of 58, while the mean path which it describes is 9,650, and the number of collisions it encounters per second amount to 17,750 millions.

of chlorine. On analysis, we find that one molecular volume of hydrochloric acid gas yields one atom of chlorine and one atom of hydrogen. The two molecular volumes of the acid gas, therefore, contain two atoms of hydrogen and two of chlorine. A molecule of hydrogen must, therefore, contain two atoms, and a molecule of chlorine two atoms. Therefore, if the atomic weight of hydrogen be assumed as unity, its molecular weight will be 2, and its molecular volume also 2.

54. Since all molecular volumes are equal, the molecular volume of any aëriform substance must be 2. The density of aëriform bodies is the relative weight of one volume; hence, the molecular weight of any aëriform body must be double its density. The molecular weights of the elements previously named are:

Hydrogen,	2.	Nitrogen,	28.	Phosphorus,	124.
Chlorine,	71.	Oxygen,	32.	Arsenic,	300.
Bromine,	160.	Sulphur,	64.	Mercury,	200.
Iodine,	254.	Selenium,	159.	Cadmium,	112.

If all the elementary molecules had the same number of atoms as the hydrogen molecule, the atomic weights of the elements would be identical with their densities. This is the case with most of the elements that can be obtained in the aëriform state. *In all cases* the molecular weight of an element is equal to the product of its atomic weight by the number of atoms in one elementary molecule. Hence, if we know any two of these quantities, we can find the other by a simple calculation.

55. The atomic weight of any element is obtained by comparing the results of the analysis of many compounds of that element. When the compound is a gas, the density is obtained by direct experiment, and the relative proportions of its constituents are easily determined.

Two volumes of each of the following compounds of hydrogen are found to yield these results:

WEIGHTS OF TWO VOLUMES	DEN-SITY	NAME OF COMPOUND	PROPORTIONS BY WEIGHT	PROPORTIONS BY VOLUME	FOR-MULÆ
36.5	18.25	Hydrochloric acid.	H, 1 + Cl, 35.5	H, 1 + Cl, 1	HCl
18.	9.	Perfect steam.	H, 1 + O, 8.	H, 2 + O, 1	H_2O
17.	8.5	Ammonia.	H, 1 + N, 4.7	H, 3 + N, 1	H_3N
16.	8.	Marsh gas.	H, 1 + C, 3.	H, 4 + C, 1	H_4C

If we consider only the weights which unite with one part of hydrogen, the atomic weight of chlorine is 35.5; of oxygen, 8; of nitrogen, 4.7; and of carbon, 3.

The molecular weight of each of these compounds is equal to the weight of two volumes. The molecular weight is also equal to the sum of the atomic weights of its constituents. If these two do not agree, the atomic weights assigned are incorrect.

The molecular weight of hydrochloric acid is 36.5: this is also the sum (35.5 + 1) of the combining weights of chlorine and hydrogen. Therefore, 35.5 is the atomic weight of chlorine.

The molecular weight of steam is 18; but the sum (1 + 8) of the combining weights is half of this; hence, one molecule of steam must contain 2 parts of hydrogen and 16 of oxygen.

So, also, 17 parts, by weight, of ammonia must contain 3 parts of hydrogen and 14 of nitrogen; and 16 parts, by weight, of marsh gas must contain 4 parts of hydrogen and 12 of carbon.

As we know of no hydrogen compounds in which chlorine, oxygen, nitrogen, and carbon unite in less proportion than 35.5, 16, 14, and 12, these numbers are adopted as the atomic weights of these elements.

56 *a*. The atomic weights of those elements which do not form aëriform compounds with hydrogen, are determined by careful analyses of their compounds with chlorine or with some element whose atomic weight is known.

We are aided in determining what number is most likely to represent correctly the atomic weight of these elements, (1) by means of the vapor density of their aëriform compounds, if they have any.

(2) By the fact that the similar salts (chlorides, sulphates, etc.), of very many elements, may be arranged in groups which have the same crystalline form. Such substances are said to be *isomorphous;*

as, for example, Mg, Zn, Cd. Now, we know the molecular weight of the cadmium salts by means of their vapor densities, and it is fair to suppose that the others have the same molecular structure and may be represented by analogous formulæ.

(3) A more general aid in determining the atomic weight of an element is by means of its specific heat. The specific heat of a body is the fraction which expresses the amount of heat required to raise a unit weight of the substance as compared with that required to raise an equal weight of water from 0° C. to 1° C. It is found that the product of the atomic weights by the specific heats of the several elements is a constant quantity, which is called the specific heat of atoms. The mean value of this product is 6.34, and any small deviation from it is thought to result from the unavoidable errors of experiment.

These relations are shown in the following table:

	SPECIFIC HEAT.		ATOMIC WEIGHT.	
Sodium,	0.29340	×	23	= 6.75
Sulphur,	0.20259	×	32	= 6.48
Arsenic,	0.08140	×	75	= 6.11
Phosphorus,	0.18870	×	31	= 5.85
Mercury,	0.03192	×	200	= 6.38
Cadmium,	0.05669	×	112	= 6.35
Zinc,	0.09555	×	65	= 6.21
Carbon,	0.45900	×	12	= 5.51
Silicon,	0.20300	×	28	= 5.68
Average, ...				6.34

56 *b*. If we divide the molecular weights of the elements by the atomic weights, we shall find the number of atoms in each molecule in the aëriform state.

Mercury, zinc, and cadmium have each one atom in a molecule. Their vapor densities are half their atomic weights, and their atomic volumes are only half those of hydrogen.

Phosphorus and arsenic have each four atoms in a molecule. Their vapor densities are double their atomic weights, and their atomic volumes are only half those of hydrogen.

Most of the other elements are supposed to contain two atoms in each molecule. Their vapor densities are equal to their atomic weights, and their molecular volume is equal to that of hydrogen.

57. If these considerations are accepted, we must represent hydrochloric acid by the formula, HCl; water, by H_2O; ammonia, by H_3N; and marsh gas, by H_4C. Each separate symbol represents (1) one atomic volume, (2) one atomic weight, and (3) the specific gravity of each element in the aëriform state referred to hydrogen as unity. (4) The numbers below each letter show how many times the atom is taken to form the compound molecule.

Each formula represents (1) one compound molecule: its molecular weight is the sum of the atomic weights of its constituents. (2) It also represents two volumes, and therefore its specific gravity, in the aëriform state, is half the molecular weight.

58. These formulæ are called *typical formulæ*, because they may be severally taken as types or examples of a large number of compounds having a similar molecular structure. Thus, we may have:

Hydrochloric Acid	Water	Ammonia	Marsh Gas
HCl	H_2O	H_3N	H_4C
Hydrobromic Acid	Hydrogen Sulphide	Hydrogen Phosphide	Hydrogen Silicide
HBr	H_2S	H_3P	H_4Si
Hydriodic Acid	Hydrogen Selenide	Hydrogen Arsenide	
HI	H_2Se	H_3As	

59. We can not fail to notice that these groups are distinguished by the number of atoms of hydrogen which combine with one atom of the other element. Chlorine has a combining power sufficient to fix one atom of hydrogen; oxygen has a combining power sufficient to fix two atoms of hydrogen; nitrogen has a

combining power of 3; carbon, of 4. Atoms which have an equal combining power are said to be equivalent, or to have the same atomicity; that is, they may replace each other, atom for atom.

Thus, if we decompose hydriodic acid by chlorine, we may represent the reaction, $HI + Cl = HCl + I$. Chlorine and hydrogen have each the same combining power. The metals — potassium, sodium, and silver — form compounds which contain one atom of chlorine. They displace one atom of hydrogen in hydrochloric acid, and are equivalent to it: $HCl + Na = NaCl + H$.

On the other hand, if we decompose water by chlorine, the reaction is, $H_2O + Cl_2 = 2HCl + O$. Two atoms of chlorine are required to displace one atom of oxygen; hence, the oxygen atom has twice the combining power of chlorine, or can fix two atoms of hydrogen. So, also, one atom of sulphur, calcium, or zinc combines with two atoms of chlorine or with one of oxygen, and has double the combining power of hydrogen, or an atomicity of 2.

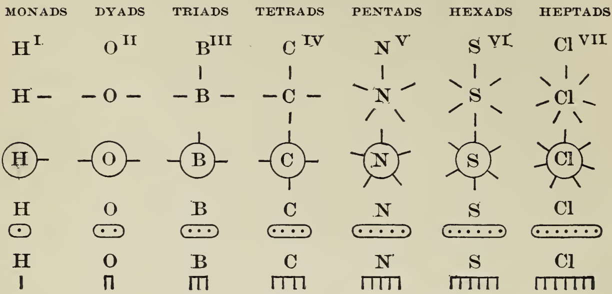
60. All the elements may be arranged in seven groups, according as they combine with 1, 3, 5, 7 atoms or 2, 4, 6 atoms of hydrogen or of chlorine. The elements which make up these groups are called:

Monads or univalent,	whose atomicity	= 1	as H'
Dyads or bivalent,	" "	= 2	as O''
Triads or trivalent,	" "	= 3	as B'''
Tetrads or quadrivalent,	" "	= 4	as C^{IV}
Pentads or quinquivalent,	" "	= 5	as N^{V}
Hexads or sexivalent,	" "	= 6	as S^{VI}
Heptads or septivalent,	" "	= 7	as Cl^{VII}

61. The equivalence or atomicity of an atom is represented by accent marks or Roman numerals placed above the symbol. These marks do not multiply the atoms, and should not be confounded with the figures placed below the symbols.

The atomicity is sometimes expressed graphically by lines called

bonds radiating from a symbol, or from some figure which represents an atom. The following are examples:



62. The atomicities of all of the elements have not been experimentally determined, and are open to revision. There are also apparent variations in the equivalency of many elements, which are difficult of explanation. Thus, nitrogen is trivalent in ammonia, NH_3, and quinquivalent in ammonium chloride, NH_4Cl. Chlorine is usually regarded as a monad element, but it appears also to act as a heptad. So, also, iron is variously classed a bivalent, quadrivalent, and sexivalent element.

Generally, but not always, the atomicity assigned to an element is that derived from its highest compound with monad elements, and any lower compound is said to be *unsaturated*, or that the element has one or more of its bonds unsatisfied. Such unsaturated compounds are frequently unstable, and tend to form the higher, saturated compound. Thus, in ferrous chloride, $Fe^{II}Cl_2$, the iron is apparently bivalent, but on exposure to the air it forms ferric compounds which are either quadrivalent or sexivalent.

$$\begin{array}{l} Fe\equiv Cl_3 \\ | \\ Fe\equiv Cl_3 \end{array} \text{ or } Fe^{IV}_2\,Cl_6 \qquad \begin{array}{l} Fe\equiv Cl_3 \\ ||| \\ Fe\equiv Cl_3 \end{array} \text{ or } Fe^{VI}_2\,Cl_6$$

We find, however, that the same element almost always exhibits a valency which may be represented either by an odd or by an even number. Those elements whose valency can be represented by 1, 3, 5, or 7, are called *perissads;* those whose valency is 2, 4, 6, or 8, are called *artiads.* It is also noticeable that the sum of the bonds, in a stable, saturated molecule, is always an *even* number.

Although there are many apparent contradictions and unexplained anomalies in the doctrine of atomicity, it bids fair to be of immense importance in theoretical chemistry.

The following table gives the atomicities usually assigned, and also groups the elements in accordance with their more striking properties.

TABLE OF THE ELEMENTS.

PERISSADS.

Monads.			Triads.		
ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Hydrogen	H	1.	Boron	B	11.
Fluorine	F	19.	Indium	In	113.4
Chlorine	Cl	35.5	Gold	Au	197.
Bromine	Br	80.	Thallium	Tl	204.
Iodine	I	127.			
			Pentads.		
Lithium	Li	7.	Nitrogen	N	14.
Sodium	Na	23.	Phosphorus	P	31.
Potassium	K	39.1	Vanadium	V	51.2
Rubidium	Rb	85.4	Arsenic	As	75.
Caesium	Cs	133.	Antimony	Sb	122.
			Bismuth	Bi	210.
Silver	Ag	108.			
			Niobium	Cb	94.
			Tantalum	Ta	182.

ARTIADS.

DYADS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Oxygen	O	16.	Copper	Cu	63.4
			Mercury	Hg	200.
Calcium	Ca	40.	Glucinum	G	9.4
Strontium	Sr	87.6	Thorinum	Th	57.9
Barium	Ba	137.	Yttrium	Y	61.6
			Lanthanum	La	93.6
Magnesium	Mg	24.	Didymium	D	95.
Zinc	Zn	65.2	Erbium	E	112.6
Cadmium	Cd	112.	Terbium	Tr	148.5

TETRADS.			HEXADS.		
Carbon	C	12.	Ruthenium	Ru	104.4
Silicon	Si	28.	Osmium	Os	199.2
Titanium	Ti	50.			
Tin	Sn	118.	Molybdenum	Mo	96.
			Tungsten	W	184.
Aluminium	Al	27.4			
Gallium	Ga.	69.9	Sulphur	S	32.
Zirconium	Zr	89.6	Selenium	Se	79.4
			Tellurium	Te	128.
Cobalt	Co	58.8			
Nickel	Ni	58.8			
Cerium	Ce	92.	Chromium	Cr	52.2
Uranium	U	120.	Manganese	Mn	55.
Lead	Pb	207.	Iron	Fe	56.
Palladium	Pd	106.			
Platinum	Pt	197.4			
Rhodium	Rh	104.4			
Iridium	Ir	198.			

NOTE. — This list is taken from "Watt's Dictionary of Chemistry." The atomic weights do not always accord with those given on pp. 12 and 13.

63. We may suppose that the elementary molecules consist of two atoms whose bonds mutually satisfy each other, graphically represented thus:

$H-H$, Hydrogen. $O=O$, Oxygen. $N\equiv N$, Nitrogen.

In compounds, any atom may have its bonds satisfied by another atom having an equal atomicity; or by sev-

eral atoms, the sum of whose bonds is equal to that of the first; thus, a dyad may be saturated by two monad atoms or by one dyad atom; a triad by a triad, by three monads, or by one monad plus one dyad, etc. Thus, we may represent graphically:

Mercuric oxide, $Hg''=O''$

Water, $H'-O''-H'$

Sodium hydrate, $Na'-O''-H'$

Carbonic anhydride, $O''=C^{IV}=O''$

Ammonia,
$$\begin{array}{c} H' \\ | \\ H'-N'''-H' \end{array}$$

Marsh gas,
$$\begin{array}{c} H' \\ | \\ H'-C^{IV}-H' \\ | \\ H' \end{array}$$

64. In compounds, a portion of the bonds of a multivalent atom may be satisfied by another atom of the same element. Examples of this may be represented graphically, thus:

Mercurous oxide,
$$\begin{array}{l} Hg'' \\ \mid \quad >O'' \\ Hg'' \end{array}$$

Mercurous chloride,
$$\begin{array}{l} Hg''-Cl' \\ \mid \\ Hg''-Cl' \end{array}$$

Ferrous chloride,
$$\begin{array}{l} Fe^{VI}=Cl'_2 \\ |||| \\ Fe^{VI}=Cl'_2 \end{array}$$

Ferric chloride,
$$\begin{array}{l} Fe^{VI}\equiv Cl'_3 \\ ||| \\ Fe^{VI}\equiv Cl'_3 \end{array}$$

65. The theory of atomicities has received an important extension in the doctrine of *radicals.*

Suppose an atom of hydrogen were removed from the saturated molecules, HCl, H_2O, H_3N, H_4C: there would remain, Cl, HO, H_2N, H_3C. These residues are evidently unsaturated, and are able to combine with an atom of hydrogen to reproduce the original compound, or with any other monad to form such compounds as, Cl_2, KCl, KHO, KH_2N, H_3ClC. Such unsaturated residues, or groups of atoms, are called *radicals.*

Compound radicals act precisely like the elements: they do not generally exist in a free state in nature, but sometimes may combine with a similar group to form saturated molecules. If but one hydrogen atom is removed, the radical is univalent; if two, bivalent; if three, trivalent; and so, generally, the equivalence of the radical is the number of unsatisfied bonds.

From marsh gas we may derive four radicals, and obtain by their union with elementary atoms, or with other radicals, a great number of compounds. Thus, we may have from H_4C, = marsh gas, a saturated compound.

		FORMING COMPOUNDS WITH	
RADICALS.	NAME.	CHLORINE.	OTHER RADICALS.
$(CH_3)'$ univalent	Methyl	CH_3Cl, methyl chloride	$(CH_3)_2$, free methyl.
$(CH_2)''$ bivalent	Methylene	CH_2Cl_2, methylene chloride.	$(CH_2)_2O_2$, dioxymethylene.
$(CH)'''$ trivalent	Formyl	$CHCl_3$, chloroform.	CHO, O, C_2H_5, formic ether.
$(C)^{IV}$ quadrivalent	Carbon	CCl_4, tetra-chloride of carbon.	CH_4, marsh gas.

66. The term radical is further applied to any group of atoms which is common to a series of allied compounds. We may thus have an almost infinite series of radicals, which are for the most part purely hypothetical, and which we do not expect to obtain in an isolated form. Among those recognized in inorganic chemistry, that have received names, are the following:

$(HO)'$	hydroxyl.	$(NO_2)'$	nitryl.
$(HS)'$	hydrosulphuryl.	$(NO)'$	nitrosyl.
$(H_4N)'$	ammonium.	$(SO_2)''$	sulphuryl.
$(H_2N)'$	amidogen.	$(CO)''$	carbonyl.
$(CN)'$	cyanogen.	$(PO)'''$	phosphoryl.

The names of all compound radicals, except the three given above, end in *yl.* The radicals recognized in organic chemistry are so numerous that this branch of the science has been called the chemistry of compound radicals.

67. The nomenclature and notation of compounds are at present in a confused state. This arises from the

fact that two principal systems are in common use: the older, devised by Lavoisier and Berzelius, is based mainly on the structure of the oxygen compounds, and regards all ternary oxides as made up of two groups of binary oxides; as, $BaO + SO_3 = BaO, SO_3$. This is called the *dualistic* system.

The newer system regards every molecule as a unit; as, $BaSO_4$, and is called the *unitary* or *molecular* system.

68. Formulæ are called *empirical* when they simply express the results of analysis in atomic symbols, without endeavoring to denote the manner in which the atoms are united; and *rational*, if they endeavor to represent the manner in which the atoms are grouped together in a compound. There can be but one empirical formula of a substance, but there may be as many rational formulæ of any compound as there are different views respecting its molecular structure. The principal of these rational formulæ are: (1) the *dualistic*, representing the theory of Berzelius; (2) the *typical*, in which the grouping is referred to representative compounds called types; such as, H_2, HCl, H_2O, H_3N, H_4C; and (3) the *structural*, which are an extension of the typical by including the compound radicals. All of these formulæ are useful; but the student must bear in mind that no one of them represents the actual position or grouping of the atoms in a complex formula with absolute certainty. Its terms are thus defined:

69. According to the dualistic theory, all binary oxides may be classed in three groups: bases, indifferent bodies, and acids.

Bases are electro-positive binaries, which are formed by the union of oxygen with a metal. Acids are electro-negative binaries, which are generally formed by the union of oxygen with a non-metal. The soluble acids have a sour taste, and redden litmus paper; the soluble bases have frequently an acrid taste, and restore the color

of reddened litmus paper. The strongest bases are called the alkalies: they are the oxides of the potassium group.

The two groups are further characterized by the fact that they combine together to form ternary compounds called *salts*. Thus, BaO is a base, barium oxide; SO_3 is an acid, sulphuric acid. Both these may be obtained in an isolated form. If they are heated together they form BaO, SO_3, which is a salt called barium sulphate.

An indifferent body is one that either (1) will combine with no other, or (2) that sometimes plays the part of a base and sometimes that of an acid. Water is an indifferent body: it combines with barium oxide to form barium hydrate, BaO, H_2O; it also combines with sulphuric anhydride to form hydric sulphate, H_2O, SO_3.

70. The later theories use the same terms, but with a different meaning. Oxides that do not contain hydrogen are called *anhydrides.* The metallic oxides, like K_2O, CaO, HgO, are called *basic anhydrides;* and the non-metallic oxides, like SO_3, N_2O_5, are called *acid anhydrides.* These are named like other binary compounds:

BASIC ANHYDRIDES.		ACID ANHYDRIDES.	
Na_2O	Sodium oxide.	SO_2	Sulphurous anhydride.
Ag_2O	Silver oxide.	SO_3	Sulphuric anhydride.
BaO	Barium oxide.	Cl_2O	Hypochlorous anhydride.
CaO	Calcium oxide.	Cl_2O_3	Chlorous anhydride.
FeO	Ferrous oxide.	N_2O_3	Nitrous anhydride.
Fe_2O_3	Ferric oxide.	N_2O_5	Nitric anhydride.
Hg_2O	Mercurous oxide.	I_2O_5	Iodic anhydride.
HgO	Mercuric oxide.	I_2O_7	Periodic anhydride.

71. These anhydrides may combine with water, forming *hydrates.* Formerly it was supposed that these hydrates contained the water molecule, H_2O; but now it is generally thought that they bear only a typical relation to water, containing, perhaps, its radical hydroxyl; thus, $BaO + H_2O = Ba(OH)_2$; $SO_3 + H_2O = SO_2(OH)_2$.

In accordance with this view, a basic hydrate is a compound of hydrogen and a positive atom or radical

united by oxygen. These hydrates are formed on the type of one or more molecules of water.

Type, H_2O.	Type, $2H_2O$.
$\left.\begin{matrix} K' \\ H' \end{matrix}\right\} O''$ Potassium hydrate.	$\left.\begin{matrix} Ca'' \\ H'_2 \end{matrix}\right\} O''_2$ Calcium hydrate.

Or we may consider these bodies as compounded with hydroxyl; thus, K–OH; $Ca''(OH)'_2$, as if derived from water, H–OH, taken as often as is necessary.

72. All true acids are compounds of hydrogen with a negative atom or radical. In the binary acids, like HCl, HI, this union is direct. These acids all receive the termination *ic*, as HCl, hydrochloric acid. In the ternary acids the union is effected by a linking atom of oxygen.

Some acids are formed on the type of one molecule of water; as:

Nitric acid, H_2O, N_2O_5 or HNO_3 or $\begin{matrix} NO'_2 \\ H' \end{matrix}\!\!>O''$ or $(HO)'NO'_2$.

Nitrous acid, H_2O, N_2O_3 or HNO_2 or $\begin{matrix} NO' \\ H' \end{matrix}\!\!>O''$ or $(HO)'NO'$.

Others are on the type of two molecules; as, $(H_2O)_2$:

Sulphuric acid, H_2O, SO_3 or H_2SO_4 or $\begin{matrix} SO''_2 \\ H'_2 \end{matrix}\!\!>O''_2$ or $(HO)'_2SO''_2$.

Sulphurous acid, H_2O, SO_2 or H_2SO_3 or $\begin{matrix} SO'' \\ H'_2 \end{matrix}\!\!>O''_2$ or $(HO)'_2SO''$.

A few are on the type of three molecules; as, $(H_2O)_3$:

Phosphoric acid,

$3H_2O$, P_2O_5 or H_3PO_4 or $\begin{matrix} PO''' \\ H'_3 \end{matrix}\!\!>O''_3$ or $(HO)'_3PO'''$.

We may also suppose these acids to be formed by the union of hydroxyl with a negative radical, as in the last formula given in each of the above.

73. These acids are all named from the negative radical. If only two acids of an element are known, the stronger equivalence is indicated by the suffix *ic*, and the weaker by *ous*. If four acids exist, the prefix *per* is placed before the higher *ic* acid, to indicate the highest combination, and the prefix *hypo* before the lower *ous* acid, to indicate the lowest. Generally these suffice: the other acids, if any, are indicated by arbitrary names.

We have the following acids of chlorine and of sulphur:

HCl	Hydrochloric acid.	H_2S	Hydrosulphuric acid.
$HClO$	Hypochlorous acid.	H_2SO_2	Hyposulphurous acid.
$HClO_2$	Chlorous acid.	H_2SO_3	Sulphurous acid.
$HClO_3$	Chloric acid.	H_2SO_4	Sulphuric acid.
$HClO_4$	Perchloric acid.		(See p. 115).

74. A salt is formed by the substitution of a metal for the hydrogen in an acid. Binary compounds like KI, KCl, NaCl are called *haloid salts*, from their resemblance to the last named, which is common salt. Their names all end in *ide*, as before described.

The salts which contain oxygen are ternary compounds, and are called *oxy-salts*. These derive their names from the acids from which they are formed, only changing *ic* to *ate*, and *ous* to *ite*, and prefixing the name of the basic element or radical. Thus:

$KClO$	Potassium hypochlorite,	or hypochlorite of potassium.
$KClO_2$	Potassium chlorite,	or chlorite of potassium.
$KClO_3$	Potassium chlorate,	or chlorate of potassium.
$KClO_4$	Potassium perchlorate,	or perchlorate of potassium.

75. Acids are said to be monobasic, bibasic, tribasic, etc., according to the number of hydrogen atoms they contain that may be replaced by a positive atom. Thus, sulphuric acid is bibasic, because it has two replaceable atoms of hydrogen. If one is replaced by a monad, an

acid salt is formed; if both are replaced either by two monads or by one dyad, a *normal* salt is formed. For example:

$KHSO_4$	is the acid potassium sulphate (or bisulphate).
K_2SO_4	is the normal potassium sulphate.
$Pb''SO_4$	is the normal lead sulphate.
$Al_2'''(SO_4)_3$	is the normal aluminium sulphate.

76. Double salts are those in which the hydrogen atom is replaced by atoms of two different metals.

The alums are familiar examples. Thus, common alum has the following composition:

$$Al_2O_3,\ 3\,SO_3 + K_2O,\ SO_3;\ \text{or}\ Al_2K_2S_4O_{16};\ \text{or}\ AlK,\ (SO_4)_2.$$

The haloid salts also form double salts* which are ternary. The double chloride of potassium and platinum has the formula:

$$2\,KCl,\ PtCl_4,\ \text{or}\ K_2PtCl_6,\ \text{or}\ (KCl)_2,\ Cl''_2(PtCl_2).$$

77. Sulphur acts like oxygen as a linking atom, and there exists a series of sulphur compounds analogous to those already given of oxygen. Thus:

		OXYGEN ANALOGUES.
K_2S	is a basic sulpho-anhydride.	K_2O
SnS_2	is an acid sulpho-anhydride.	SnO_2
H_2S	is a sulpho-acid.	H_2O
HS	is its radical.	HO
KHS	is a sulpho-base.	KHO
H_2SnS_3	is a sulpho-acid.	H_2SnO_3
$K_2S,\ SnS_2$, or K_2SnS_3,	is a sulpho-salt.	K_2SnO_3

There are other series of less importance; we mention only that derived from hydrofluosilic acid, $2HF,\ Si,\ F_4$, in which the hydrogen may be replaced by metals; as, $2KF,\ SiF_4$ or $K_2\ SiF_6$.

78. When salts are dissolved in water, and the solution evaporated, bodies are produced which have regular

* Such double salts of saturated bodies are called "molecular compounds." The linking chlorine appears to act diatomic.

or crystalline forms. These crystals are frequently found to contain a molecule of the salt and from 1 to 24 molecules of water. In such crystalline molecules the water is supposed to exist as such, and is called the *water of crystallization.* The water is an essential part of the crystalline molecule, but not of the chemical molecule.

This is evidenced by the fact that the same saline molecule may combine with different proportions of water to form different crystalline forms. Thus sodium carbonate crystallizes from a boiling solution as $Na_2CO_3 + H_2O$, in rectangular tables; at ordinary temperatures, as, $Na_2CO_3 + 10H_2O$, in rhombic prisms. In dry air these rhombic prisms lose their water of crystallization and crumble to a white powder. This is called *efflorescence.* Some crystals require a higher temperature to expel their water of crystallization. Blue cupric sulphate is $CuSO_4 + 5H_2O$. It loses 4 molecules of water when dried at 100° C., and does not give up the remaining molecule until it is heated to 200° C. It then forms a white powder, $CuSO_4$, and is said to be *anhydrous.* The last molecule of water is sometimes called the *water of constitution,* because it seems to be more strongly connected with the saline molecule than the others; and this is indicated by separating it from them in formulæ; thus, H_2O, $CuSO_4 + 4H_2O$.

79. The notation of compounds is their representation by means of symbols and signs. From what has already been said, it is evident that this will vary with the ideas which are intended to be conveyed. As a general rule, the positive atoms and radicals are written first. A numeral placed below a symbol multiplies it alone. A numeral placed in any other position multiplies every atom by itself until some sign of separation, as a bracket, parenthesis, or comma, is reached.

In mineral chemistry, the dualistic formulæ are of advantage when we wish to express that the same anhydride is common to several compounds; as, K_2O, CrO_3, and K_2O, $2CrO_3$ instead of K_2CrO_4 and $K_2Cr_2O_7$. In organic chemistry, the formulæ are generally structural. We contrast these systems by the following equations.

The reactions between lead nitrate and sulphuric acid:

EMPIRICAL. $PbN_2O_6 + H_2SO_4 = PbSO_4 + H_2N_2O_6.$

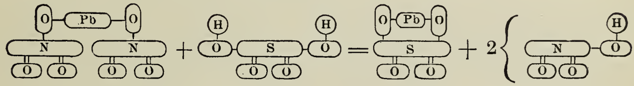
DUALISTIC. $PbO,\ N_2O_5 + H_2O,\ SO_3 = PbO,\ SO_3 + H_2O,\ N_2O_5.$

TYPICAL. $\left.\begin{matrix}(NO_2)_2\\ Pb\end{matrix}\right\}O_2 + \left.\begin{matrix}SO_2\\ H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}SO_2\\ Pb\end{matrix}\right\}O_2 + 2\left(\left.\begin{matrix}NO_2\\ H\end{matrix}\right\}O\right).$

STRUCTURAL.

$$Pb{<}{}^{O-NO_2}_{O-NO_2} + {}^{HO}_{HO}{>}SO_2 = Pb{<}{}^{O}_{O}{>}SO_2 + 2(HO-NO_2).$$

GLYPTIC.



NOTE.—The student will find it of great advantage to be enabled to use readily all systems of formulæ. In this book, although preference is given to structural formulæ, the dualistic system is still retained.

In many of the older text-books on chemistry, different atomic weights were assigned to the elements, giving rise to a different set of formulæ.

Recapitulation.

Atoms differ in—

Weight — measured relatively by the hydrogen unit.
In electrical relations — positive or negative.

In combining power:

- perissads, odd:
  - monads $'$ or univalent; as, H'.
  - triads $'''$ or trivalent; as, B'''.
  - pentads ^{V} or quinquivalent; as, N^{V}.
  - heptads ^{VII} or septivalent; as, F^{VII}.
- artiads, even:
  - dyads $''$ or divalent; as, O''.
  - tetrads ^{IV} or quadrivalent; as, C^{IV}.
  - hexads ^{VI} or sexivalent; as, S^{VI}.

Molecules are:
- composed of like atoms — elementary; as, H_2.
- composed of unlike atoms — compound; as, HCl.

Radicals are residues of molecules, and act as atoms.

They are:
- either an elementary atom, as H,
- or an unsaturated molecule, as HO.

Saturated compounds are classified

- binary oxides
  - basic anhydrides; as, K_2O.
  - acid anhydrides; as, SO_3.
  - neutral bodies; as, MnO_2, H_2O.
- basic hydrates; as, KHO.
- acids . . .
  - binary or haloid acids; as, HCl.
  - ternary acids; as, H_2SO_4.
- salts . . .
  - binary or haloid salts; as, KCl.
  - ternary salts; as, K_2SO_4.
  - double salts; as, $KAl(SO_4)_2$.

The *actual* proportion of atoms in a compound is always denoted by numerals; as, HCl, H_2O, Hg_2Cl_2, $HgCl_2$, which take the names, *prot*, 1; *bi*, 2; *ter*, 3; *tetra*, 4; *penta*, 5; *sesqui*, 2 : 3.

The *relative* proportion of atoms in the compounds of a given element, as R, is denoted by prefixes and suffixes.

The highest	equivalence	of	four	compounds	by	*per*—R—*ic*.
"	"	"	" two	"	"	R—*ic*.
The lowest	"	"	" two	"	"	R—*ous*.
"	"	"	" four	"	"	*hypo*—R—*ous*.

The termination *ide* is applied only to binaries; as, KCl.

The terminations of ternary salts are:

ite, when the acid ends in *ous;* as, K_2SO_3.
ate, " " " " " *ic;* as, K_2SO_4.

The termination of compound radicals is *yl;* as, HO.

NOTE.—Since this book was electrotyped, the London Chemical Society has advised some changes in Notation and Nomenclature,—as *hydroxide* for *hydrate* in those compounds which are supposed to contain hydroxyl, OH. Most of these changes have been made, but the student is requested to make the one mentioned for himself, or to regard the two words as synonymous.

CHAPTER IV.

WATER AND ITS ELEMENTS.

ELEMENT.	SYMBOL.	WT. OF ONE LITRE IN GRAMMES.	SPECIFIC GRAVITY.		ATOMIC WEIGHT.	DISCOVERER.
			AIR = 1.	H = 1.		
Hydrogen . .	H	.0896	.0692	1.	1	Cavendish, 1766.
Oxygen	O	1.4336	1.1056	16.	16	Priestley, 1774.
Water: Steam	H_2O	.8064	.622	9.		Investigated by
Water: Liquid	H_2O	1000.	773.	11160.		Lavoisier, 1781.

80. We have already learned that water is composed of hydrogen and oxygen, in the proportions of two volumes of hydrogen to one of oxygen, or, by weight, of 2 parts of hydrogen to 16 of oxygen.

Hydrogen.

81. Hydrogen is an essential constituent of water, of acids, and of most organic compounds.

It may be obtained from any of these bodies. From water, (1) by the electrical current (Art. **47**); (2) by passing steam over iron filings heated to redness (Exp. 29); (3) from cold water by the action of sodium (Exp. 4); (4) by placing bright zinc strips in water. In this case the zinc decomposes the water, forming zinc oxide and setting the hydrogen free: $Zn + H_2O = ZnO + \hat{H}_2$. The action soon ceases, because the zinc becomes coated with an insoluble film of the oxide, which prevents further oxidation.

(5) If, however, the water is mixed with one-fifth of its weight of sulphuric acid, the action is continuous,

because the acid unites with the oxide as fast as it is formed to produce zinc sulphate, ZnO, SO_3, which readily dissolves in the excess of water, and thereby the surface of the zinc is kept bright and clean. We may suppose that the two reactions occur simultaneously, and that the molecule of water decomposed is that previously in combination with the acid, and may represent the process by a single equation:

$$Zn + H_2O, SO_3 = ZnO, SO_3 + \overset{\frown}{H}_2.$$

If too little water is present, a sulphate is produced which is with difficulty soluble, and the action is less energetic.

82. A convenient apparatus is shown in Fig. 20: a represents a flask containing a handful of granulated zinc;* b is a funnel reaching almost to the bottom of the flask, through which the acidulated water may be poured as required; and c is a tube just passing through the cork for the escape of the gas. The end of the tube, d, may be placed under a receiver, as the cylinder e. The cylinder is first to be filled with water and inverted in a suitable cistern also containing water. As the hydrogen, at first, is mixed with the air of the flask, none of the escaping gas should be employed in experiments *until the air has been thoroughly expelled from the apparatus.* The moment when this result is reached may be ascertained by filling test tubes with the escaping gas in the water cistern, and, after lifting them carefully from the water without changing their vertical position, applying a lighted match to the mouth of the tube. If the hydrogen is free from air, it will burn quietly; but if much air is present, the mixture will be ignited with a sharp explosion.

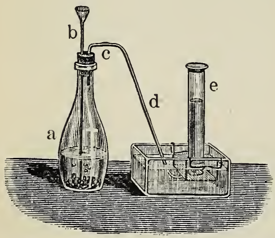


FIG. 20.

* Zinc is granulated by melting zinc scraps in an iron ladle, and slowly pouring the molten metal from a height into a pail filled with cold water.

NOTE.—When explosions are anticipated in the process of experiment, the quantities operated on should be small; and, in the case of gases, the vessels in which they are contained should be of thick glass. Even in this case, it is prudent to wrap glass vessels in a thick towel before applying the match.

The hydrogen obtained from zinc is liable to certain impurities, which may be sufficiently removed by passing the gas through three bottles containing, respectively, (1) a dilute solution of sodium hydrate, (2) a dilute solution of silver nitrate, and (3) small lumps of charcoal. A fourth wash bottle, containing strong sulphuric acid, may also be used to dry the gas.

The dry gas may be collected over quicksilver, or used in experiments which require only a stream of the gas. The fourth bottle is unnecessary when the hydrogen is collected over water.

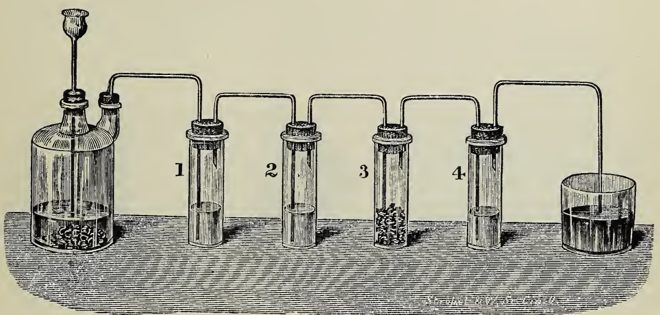


FIG. 21.

83. The Physical properties of hydrogen make it a convenient standard for the density of aëriform bodies. Hydrogen is 14.43 times lighter than air. It is a colorless, odorless, tasteless gas which has been liquefied under a pressure of 280 atmospheres. When this liquid was allowed to expand suddenly, the cold produced was sufficient to condense a portion to a fine spray containing solid particles which rattled like shot.

Exp. 62.—Prepare a solution of soap, and, by means of a tobacco pipe connected with the evolution tube, inflate soap bubbles with hydrogen. When detached from the pipe they rise rapidly, showing that *hydrogen is lighter than air*. Small bags made of caoutchouc and filled with the gas will rise like a balloon.

Owing to its lightness, jars may be filled with the gas by *displacement.*

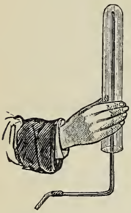


FIG. 22.

Exp. 63.—This may be done by fitting a vertical tube to a flask from which the gas is escaping rapidly, and by holding over this a dry cylinder (Fig. 22). After a few minutes, the hydrogen will be found to have so completely displaced the air of the cylinder that no explosion will ensue when a lighted taper is applied to the mouth of the cylinder.

Exp. 64.—So, also, hydrogen may be poured from one cylinder to another (Fig. 23), if we only remember that in pouring hydrogen the gas will flow *up*, and not down as is the case in pouring water. Unless the receiving cylinder is much smaller than the other, all its air will not be displaced, and now an explosion may be expected when a lighted taper is applied at its mouth.

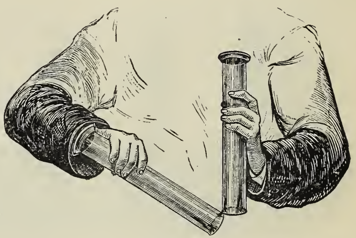


FIG. 23.

84. Hydrogen is taken as the unit of atomic weights. Its rate of diffusion is the highest known. This is due to its high rate of molecular motion. (See note to p. 52). It diffuses 3.8 times faster than air.

Exp. 65.—Close the mouth of a glass funnel having a long delivery tube by a septum of plaster of Paris. This may be done by making a moderately thick paste of the plaster with water on a plate, inverting the mouth of the funnel therein, then suffering the plaster to harden and to dry thoroughly. Detach the funnel from the plate, and place the open tube in colored water, inverting over the closed mouth a jar filled with hydrogen. The hydrogen diffuses into the funnel faster than the air diffuses out, and soon bubbles of gas escape through the water. Now remove the jar, and the hydrogen will escape in the contrary direction, leaving a partial vacuum in the funnel, which becomes manifest by the rise of water in the tube.

A beautiful modification of this is shown in Fig. 24. A large diffusion tube is attached to a two-necked flask, which has a tube extending through the second neck below the surface of some water contained in the flask. If the septum is dry and the fittings are air-tight, a fountain of water will be formed of considerable height.

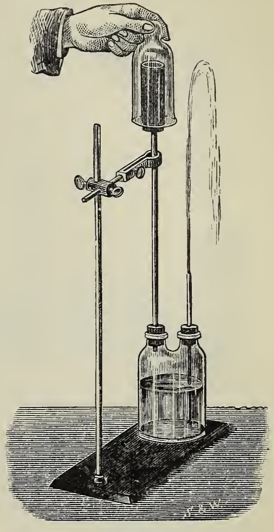


FIG. 24.

Exp. 66.—A curious experiment which shows that sound is much enfeebled in hydrogen may be performed by filling the lungs of the experimenter with *pure* hydrogen and his then attempting to speak. The voice will be weak and piping.

85. Chemical properties. The following experiments illustrate some of the chemical properties of hydrogen.

Exp. 67.—Fill a cylinder with dry hydrogen, and introduce into this a lighted wax taper. (Fig. 25.) The gas will be enkindled at the mouth of the cylinder. If the taper is pushed up into the cylinder, its flame will be extinguished. On withdrawing the taper, it may be again ignited by the burning gas, then again extinguished by passing it upward into the gas, and then rekindled for several times in succession.

FIG. 25.

This shows that hydrogen burns when in contact with the air, but that it does not support ordinary combustion.

Exp. 68.—Attach to the drying bottle a vertical tube drawn out so as to yield a small jet, as in Fig. 26. If the jet of gas be ignited, it will burn with an almost non-luminous flame. Hold over this flame an evaporating dish containing ice. The outside of the dish will become covered with moisture, and in a short time will yield drops of water.

This experiment may be modified by burning the jet within a wide glass tube. The upper part of the tube will be covered with condensed water. At the same time, a musical note will be produced, which will vary in pitch as the tube is raised or lowered. The sound is due to a series of small explosions in rapid succession, which produce regular vibrations in the air column of the tube.

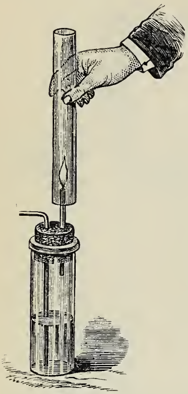


Fig. 26.

86. The product of the combustion of hydrogen in air is water. From this fact the gas derives its name. The reason why the flame is so feebly luminous is that neither the particles of the gas nor of the steam which is formed become incandescent. The flame is nevertheless very hot.

Exp. 69.—Hold in the flame a solid body, as a thin platinum wire or a bit of chalk sharpened to a point. The solid particles will soon become white hot, and the flame increase perceptibly in illuminating power.

The heat evolved by the combustion of one gramme of hydrogen is 34462 thermal units. The temperature attained, under favorable conditions, is very nearly 2800° C.

87. Hydrogen is a powerful reducing agent.

Exp. 70.—If the dry gas be passed through a tube containing cupric oxide kept at a low red heat, metallic copper will be produced. (Fig. 27.) The oxygen previously combined with the copper unites with the hydrogen to form steam. (See Exp. 30).

88. Hydrogen acts energetically in what is known as the *nascent state;* that is, at the moment that it is set free, and before it becomes perceptible to the eye.

Exp. 71.—Place in a beaker a strip of zinc; place upon this silver chloride (Exp. 57), and cover both with very dilute hydro-

chloric acid. In a few hours the silver will be reduced to the metallic state through the union of its chlorine with the hydrogen set free by the action of the acid upon the zinc.

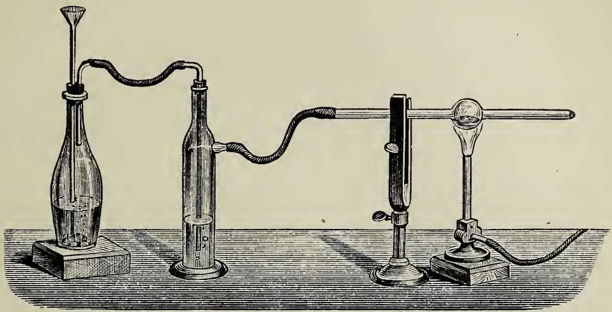


FIG. 27.

89. **Hydrogen is absorbed,** or "occluded," by many metals in large quantities. Palladium absorbs 935 times its volume of hydrogen, and forms a substance which is apparently an alloy. For this reason Graham inferred that hydrogen is a metal.

TESTS.—Hydrogen may be recognized by its physical properties and by its combustibility, but more certainly by the fact that two volumes of the gas mixed with one volume of oxygen, and exploded, form water.

90. **Physiological properties.** Although the lungs may be filled once with pure hydrogen without danger, it does not support respiration. Small animals confined in it speedily die.

91. **The only uses** which have been made of hydrogen are: (1) as a source of heat in melting platinum and other refractory metals; (2) to render the calcium employed in the Drummond light highly incandescent; and (3) as a material for filling balloons.

Oxygen.

92. Oxygen is found uncombined in the air, and is a constituent of water, of most minerals, and of many organic bodies, like sugar, starch, and alcohol.

It may be obtained, (1) by the electrolysis of water (Art. **47**), and (2) by heating many of the higher oxides, as, HgO, MnO_2, Pb_3O_4, I_2O_5. (See §§ **413, 507**).

It is most conveniently prepared by heating potassium chlorate, $KClO_3$. One gramme of this salt yields 273.8 cubic centimetres of oxygen, and a residue of 6 decigrammes of potassium chloride, $KClO_3 = KCl + 3\overset{\frown}{O}$. At a gentle heat, one-third of the oxygen is given off—$2KClO_3 = KClO_4 + KCl + \overset{\frown}{O}_2$—and potassium perchlorate is formed. This body at a higher temperature also decomposes and yields the remaining oxygen—$KClO_4 = KCl + \overset{\frown}{O}_4$—but the gas is evolved so rapidly that considerable dexterity is required in manipulation. Where large quantities are required, it is better to use a mixture of equal parts of manganese dioxide and potassium chlorate. The reaction is the same as before. The manganese dioxide is not decomposed, but by its presence regulates the action, and the mixture requires less heat than the chlorate alone.*

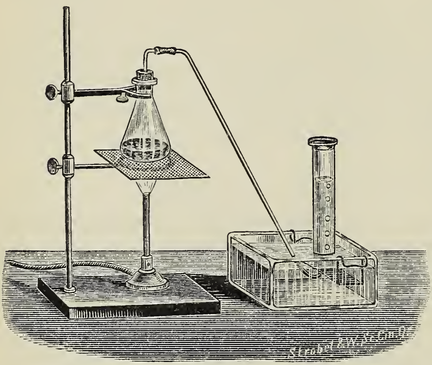


Fig. 28.

The process may be conducted in a stout glass flask, as shown in Fig. 28. A retort of iron or copper is very convenient.

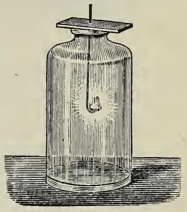
* It is advisable to heat the manganese dioxide to redness, and then cool it before using, because, if it contains carbon, explosive compounds are sometimes formed.

93. Physical properties. Oxygen may be collected over water, as 100 volumes of water, at 15° C., absorb but 3 of this gas. It is colorless, odorless, and tasteless, and has recently been liquefied under a pressure of 320 atmospheres.

94. Chemical properties. Oxygen forms compounds with all of the elements except fluorine. We have seen that ordinary combustion is due to the union of bodies with oxygen. Any substance which will burn in air will burn far more brilliantly in pure oxygen; others, that are generally considered incombustible, burn with violence in oxygen.

Exp. 72.—Having lighted a small taper, blow it out so as to leave a small spark on the wick. Plunge this into a jar of oxygen. It will be immediately rekindled. It may then be again blown out and rekindled so long as the gas remains.

Exp. 73.—Place a little sulphur in a deflagrating spoon; kindle this in the flame of a lamp and plunge it into a jar of oxygen. The sulphur will burn with a lilac flame.



Fig, 29.

Exp. 74.—Repeat the last experiment with a small piece of dry phosphorus,* and ignite it by a hot wire. On plunging it into the oxygen, it will burn with dazzling brilliancy.

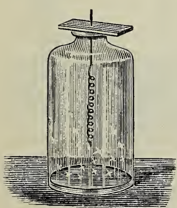


Fig. 30.

Exp. 75.—Coil an iron wire into the form of a spiral by winding it around a pencil. Pass one end through a cork which fits the mouth of the jars used, and tip the other with melted sulphur or tinder. Set fire to the tinder and plunge the wire into a jar of the gas. The iron will take fire and burn, throwing out bright sparks.

Steel gives more brilliant effects. A broken watch spring, straightened by heating so as to destroy its temper, may be used instead of the iron wire.

These experiments may be extended by using, (1) on the spoon, a pellet of napthalene or of potassium; (2) attached to a wire, a

* Phosphorus should neither be handled nor cut except under water.

bit of charcoal, or strips of zinc, thin copper, etc. Magnesium wire burns brilliantly even in ordinary air.

The experiments may be modified by using, instead of jars filled with oxygen, a stream of the gas. If the student does not possess a suitable gas holder, he may use large ox bladders softened in water and then well rubbed with glycerine. These bladders are to be tightly fitted with a glass tube, the air pressed out, and then inflated with oxygen. A temporary stopper for the tube may be made by slipping over the end a bit of rubber tubing, and plugging up the open end of the rubber tube with a glass rod.

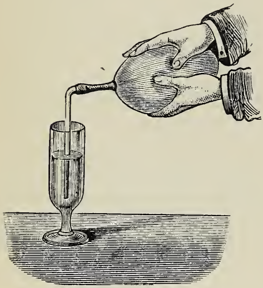


FIG. 31.

Exp. 76.—Place a pellet of phosphorus in a conical wine-glass, and pour enough hot water over the phosphorus to melt it. Now force a stream of oxygen on the melted phosphorus. It will burn under the water.

Exp. 77.—Arrange a combustion tube as shown in Fig. 32. Place in one end of the tube a bit of sulphur, or of coal, or of potassium, etc., and connect with the other end tubes plunged in empty jars to collect such products as may be volatile. Now force a stream of the gas, dried by passing it through sulphuric acid, through the tube, and ignite the bodies placed in it by heating them with the flame of a lamp. They will burn brilliantly, as in the former cases.

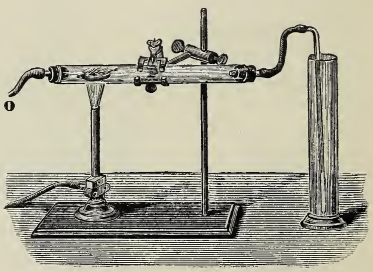


FIG. 32.

95. The products of the combustion should be tested. If a little water be poured into the jars and shaken up, the charcoal jar will be found to contain carbonic acid; the sulphur, sulphurous acid; the phosphorus, phosphoric acid. These solutions will each redden blue

litmus. The potassium residue, moistened with water, will change red litmus to blue. It is alkaline.

96. Tests for free oxygen. When oxygen is not much diluted with other gases, it may be tested by plunging into the jar containing it a splinter of pine tipped with a glowing coal. If the coal bursts into a flame, the gas is either oxygen or nitrous oxide.

Oxygen is not absorbed by potassium hydrate, but if potassium hydrate is mixed with pyrogallic acid, the alkaline pyrogallate which is formed rapidly absorbs oxygen and becomes black. This is not only a valuable test for free oxygen, but it may be used to absorb oxygen from gaseous mixtures.

Exp. 78.—Take a long tube closed at one end, and pour into it a spoonful of a solution of potassium hydrate. Now drop into the tube a few flakes of pyrogallic acid. Close the tube with the thumb, and, after shaking, invert it in a dish of water The pyrogallate will be blackened, and, on removing the thumb, the water will rise in the tube, because the oxygen has been absorbed from the air contained within it.

97. Physiological properties. If a small animal be confined in a jar of oxygen, its respiration becomes increased; it becomes feverish and soon dies, because of the too great supply of oxygen. Diluted with nitrogen, it is essential to the respiration of all animals.

Exp. 79.—Shake up a little fresh venous blood in a jar of oxygen; it will quickly become changed to red, or arterial, blood. This is the change which goes on continually in our lungs.

98. Uses of oxygen. We have already seen that oxygen is an active agent in promoting chemical changes in the laboratory of the chemist and in the greater workshop of Nature. The processes of respiration, of ordinary combustion, of fermentation, and of decay are all dependent upon it.

99. Since these various processes of oxidation consume oxygen, it may be supposed that the time might come in which the atmosphere would no longer contain it, and, therefore, that respiration would become impossible and animal life cease. Lehmann has calculated that the air contains enough oxygen to last 800,000 years; but the agencies of nature so balance each other that the proportions of the atmosphere remain unchanged.

The principal products of combustion and respiration are carbonic anhydride and water. These are necessary to the growth of plants. They consume them to form the materials which we use for food and fuel. The green parts of the plants evolve, in the sunlight, the oxygen required for animal life.

Exp. 80.—Place a handful of fresh green leaves in a bell glass. Fill this completely with water, and invert on a plate also containing water. Now expose the leaves to the bright sunlight for several hours. Bubbles of gas will collect in the upper portion of the glass, which on examination will prove to be *oxygen.*

100. The oxy-hydrogen blowpipe is one of the most efficient artificial sources of heat and light. This is an apparatus so contrived that two volumes of hydrogen are burned with one volume of oxygen. It is exceedingly dangerous to ignite large quantities of these gases previously mixed; hence, a double jet is used, as shown in Fig. 33.

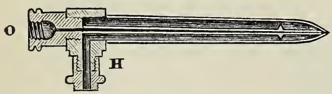


FIG. 33.

The interior jet, O, supplies a stream of oxygen, and the outer jet, H, a stream of hydrogen. The hydrogen is first turned on and enkindled; the oxygen is then forced through the hydrogen flame, and the two gases burn at the moment of mixing.

If both gases are pure and dry, the flame is feebly luminous, but intensely hot. Strips of iron, copper, zinc, etc., burn with great brilliancy in it. Metals like

antimony and arsenic are exposed to its action by supporting them on bits of charcoal. All the metals, without exception, are melted by it. By directing this jet into the interior of a small furnace lined with lime, Deville has succeeded in melting 100 kilogrammes of platinum at a single charge.

If the jet be directed on the stem of a clay tobacco pipe, it fuses. Lime does not fuse in the jet, but becomes so highly incandescent as to yield a very pure white light of dazzling brilliancy. This, properly mounted in the focus of a concave mirror, has been used for signalling, under the name of the Drummond, or calcium, light. It has been seen at a distance of more than 100 miles.

Exp. 81.—Inflate soap bubbles with a mixture of two volumes of hydrogen and one of oxygen. *After* they have risen from the jet, apply a lighted taper. A bubble the size of a tumbler will explode with a loud report.

Such mixtures of oxygen or of air with hydrogen or illuminating gas, or with the vapors of coal oils, are dangerously explosive.

101. Ozone. Whenever an electrical machine is in operation, a pungent odor is developed in the air through which the sparks pass. The same odor is perceived when a clean stick of moistened phosphorus is allowed to remain for two hours in a large flask loosely stoppered. In both cases the odor is due to a change effected in the oxygen of the air, by which it becomes remarkably energetic. This modification of oxygen is called *ozone*. Ozone may also be prepared by shaking a little ether in a jar so as to fill it with vapor, and then plunging a heated glass rod into the jar.

No method has been devised of obtaining ozone pure. It is always mixed with common oxygen, but has been obtained by induced electricity in as great a proportion as 15 per cent. Even two per cent will suffice to exhibit its wonderful properties.

102. Physical properties. Ozone is condensed oxygen. It is re-converted by heat into ordinary oxygen with a permanent increase of volume. Its specific gravity is probably $1\frac{1}{2}$ times that of oxygen: hence, a molecule of ozone contains three atoms of oxygen, while the molecule of ordinary oxygen contains two atoms.*

103. Chemical properties. Ozone is the most energetic oxidizer known. Even in the dilute state it is capable of bleaching indigo, oxidizing silver and other metals, and displacing hydrogen from its compounds with sulphur and iodine. Caoutchouc and other organic substances are quickly corroded by it.

TESTS.—When ozone acts upon potassium iodide, potassium oxide is formed and iodine is liberated.† Hence, we may use this reaction in two ways as a test for ozone.

Exp. 82.—(1) Moisten red litmus paper with a solution of potassium iodide; when the potassium oxide is formed by the ozone, it colors the paper blue. (2) Moisten unsized paper with a dilute solution of potassium iodide, containing a little boiled starch. The iodine set free by the ozone colors the starch blue. If much ozone is present, the iodine changes to iodic anhydride I_2O_5, and the paper is again bleached.

104. Ozone is frequently found in the atmosphere. This ozone is probably produced by the processes of oxidation which are every-where going on in nature. The slow oxidation of turpentine and of many ethereal oils is attended by the production of ozone, especially if these bodies are exposed to the sunlight.

105. Uses. The bleaching power of the air is due to the ozone which it contains. The atmospheric ozone destroys the malarious exhalations which arise from decaying animal and vegetable matters. It is difficult to over-rate its usefulness as a disinfecting agent.

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* Oxygen, $O{=}O$; Ozone, $\overset{O}{\overset{/\backslash}{O{-}O}}$. † $2KI + O = K_2O + \underline{2I}$. $K_2O + H_2O = 2KHO$.

It has been noticed that when the air is charged with ozone, epidemic diseases, like cholera, have abated. Conversely, air highly charged with ozone is irrespirable. It attacks the organs of respiration and produces coughing; hence it is supposed to assist in producing epidemics of catarrh and influenza.

106. Antozone. Some suppose that whenever ozone is formed, another modification of oxygen is also produced. This is called *antozone.* Its molecule contains but one atom. The white clouds which are formed when ozone is liberated in the presence of water are supposed to be due to the peculiar property which antozone has of forming clouds or mists with water. The existence of antozone is, however, still questioned.

107. Oxygen has at least two modifications, ordinary oxygen and ozone. Although these have different properties, one may be converted into the other without loss of weight. Several other elements occur in different states. These different states are said to be *allotropic* forms of the element; the word allotropy signifying *of a different character.*

Water or Hydrogen Oxide, H_2O.

108. Water is seldom found pure. The rain that falls in open fields near the end of a long shower is very nearly pure water. Although the great part of the water of our globe occurs in its free state, it enters largely into mineral combinations, and is, besides, essential to vegetable and animal structures.

109. We have shown that water is formed by the union of oxygen with hydrogen. It is one of the products formed when an organic substance containing hydrogen is burned in air. It is prepared sufficiently

pure for practical purposes by the distillation of ordinary water.

Fig. 34 represents an apparatus that may be used for this purpose. A is a capacious flask in which rain or well water is boiled: the escaping steam is cooled by passing through a *condenser*, B.

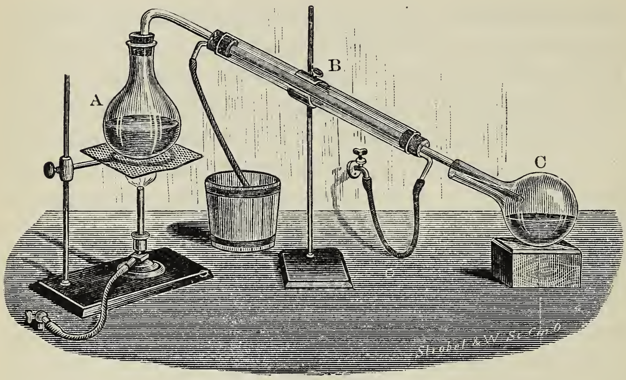


FIG. 34.

The form in the figure is known as Liebig's condenser. It is kept constantly cool by a stream of cold water entering at the bottom and flowing out at the top. The product of the distillation, which is called the *distillate*, is collected in the receiver, C. The first portions of the distillate are thrown away, and the process is stopped when about four-fifths of the water has passed over.

110. Physical properties. At ordinary temperatures, water is a tasteless, odorless liquid. When seen through a depth of several yards, it has a bluish color. It is assumed as the standard for specific heat. One cubic centimetre (Fig. 35) of distilled water at 4.1° C., its point of greatest density, is taken as the unit of weight in the metrical system. This unit is called one gramme = 15.4 grains. At this temperature it is taken as the standard of specific gravity for solids and liquids.

The freezing and boiling points of water, under the pressure of one atmosphere, are taken as standards of temperature. Water freezes to ice at a temperature of 0° C., and increases about one-tenth in volume. It evaporates at all temperatures, and so rapidly at 100° C. that it is said to boil. Steam at 100° C. occupies 1696 times the volume of the water from which it was formed.

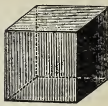


FIG. 35.

111. Chemical properties. When certain crystals are heated they give off water. The water in them appears to have one of two functions: (1) If it is easily expelled by heat, it forms part of the physical molecule, and is called the *water of crystallization;* (2) if it requires considerable heat to expel it, it forms part of the chemical molecule, and is called the *water of constitution.*

Thus, when ferrous sulphate is heated to 114° C., six molecules of the water of crystallization are driven off. On heating to 280° C., another molecule of water is driven off, which is the water of constitution. To express these different functions, we may write the formula of ferrous sulphate, $H_2O, FeO, SO_3 + 6\,H_2O$.

Some anhydrides, as K_2O or SO_3, so firmly unite with water, that heat alone will not again separate them: $K_2O + H_2O = 2KHO$; $SO_3 + H_2O = H_2SO_4$. These bodies are collectively spoken of as *hydrates*, and it seems probable that they contain water, not as such, but as the radical hydroxyl, K–HO; $(HO)'_2\,(SO_2)''$. However, some hydrates are easily decomposed by heat, as $Cu(HO)_2$, which changes to $CuO + H_2O$.

Many organic bodies, like starch, $C_6H_{10}O_5$, contain hydrogen and oxygen in the same proportions as they are found in water, and for this reason have been called *carbo-hydrates.* Nevertheless, it has not been proved that the formula of starch could be correctly written $C_6(H_2O)_5$, or that water, as such, enters into its mole-

cule. Bodies that contain neither water nor hydroxyl are said to be *anhydrous*, as KNO_3, or P_2O_5.

112. Water is specially useful to the chemist as a solvent. It dissolves a large number of bodies, and, on being evaporated, again yields them unchanged. The rain, in falling, absorbs many atmospheric constituents, and afterward, sinking into the ground, dissolves the soluble matters of the soil. If this water again comes to the surface, as spring or river water, it contains more or less solid matters, varying with the nature of the rocks through which the water flows. The ocean and isolated seas, like the Caspian, are the final reservoirs of rivers. Their waters undergo a natural distillation, yielding pure water to the clouds, and become, in consequence, more highly charged with saline matters, or become salt water. The water of the Great Salt Lake contains 12,000 grains of solid matter to the gallon. Sea water averages about 2,000 grains to the gallon. The potable waters of springs and rivers seldom contain as high as 100 grains to the gallon, and many lakes and rivers in granitic regions are very nearly pure.

113. The wholesomeness of potable waters is not so much dependent on their mineral as upon their organic constituents. If water contains ten grains to the gallon of organic matters in a state of decomposition, it is likely to be very unwholesome. Running waters are self-purifying, because their organic impurities are continually exposed to the air and are entirely decomposed. Water may be purified for drinking purposes by filtering through a thick layer of charcoal.

Distilled water is unpalatable, or "flat." The palatableness of water depends largely on its gaseous constituents. If distilled or boiled water is suffered to trickle through the air, it becomes "aërated" and more pleasant to the taste.

TESTS.—When obtainable in large quantities, water is sufficiently known by its physical properties. The presence of water in mixtures is indicated by its power of changing white anhydrous cupric sulphate to a blue color. The anhydrous cupric sulphate, $CuSO_4$, is easily formed by gently roasting "blue vitriol."

114. Hydrogen peroxide, H_2O_2, is prepared by treating barium peroxide with dilute hydrochloric acid:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

In its concentrated form it is a syrupy liquid, having a specific gravity of 1.452. It is easily decomposed into water and oxygen. It possesses remarkable oxidizing powers, changing black lead sulphide into white lead sulphate, and decomposing potassium iodide, like ozone. Hence, this reaction may also be used as a test for hydrogen peroxide. Still more remarkable is the property which it has of inducing other peroxides, when mixed with it, to yield a part of their oxygen, both bodies becoming reduced at the same moment. Thus, when hydrogen peroxide is poured upon manganese dioxide, both bodies evolve oxygen:

$$MnO_2 + H_2O_2 = MnO + H_2O + \widehat{O_2}.$$

Recapitulation.

Hydrogen is the lightest of the elements. It is taken as the standard unit:

(1) For the specific gravity of gases.
(2) For atomic and molecular weights.
(3) For molecular volumes.
(4) For atomicity, or unit of combining power.

The basicity of an acid is the amount of hydrogen it contains that may be replaced by a metal.

Hydrogen also seems to stand midway between the metals and the other elements.

Oxygen is the most abundant element, and is strongly electro-negative.

Its compounds are:

Basic, with most of the electro-positive elements.
Acid, with most of the electro-negative elements.
Indifferent, with metallic peroxides and H_2O.

Water is proved to have the formula H_2O, both by analysis and synthesis. (Arts. **46** and **47**).

It is an indifferent body, acting—

Basic, with negative anhydrides; as, H_2O, SO_3.
Acid, with positive anhydrides; as, K_2O, H_2O.

In compounds, it may be regarded as present—

(1) As water of crystallization, $Na_2B_2O_7 + 10\,H_2O$.
(2) As water of constitution, $H_2O, FeSO_4 + 6\,H_2O$.
(3) Represented by its radical hydroxyl; as, K–HO; $(HO)_2(SO_2)''$.

CHAPTER V.

THE CHLORINE GROUP (HALOGENS).

ELEMENT.	STATE AT 15° C.	SYMBOL.	SPECIFIC GRAVITY. $H_2O = 1$.	IN AËRIFORM STATE. SPECIFIC GRAVITY. AIR = 1.	H = 1.	ATOMIC WEIGHT.	DISCOVERER.
Fluorine	Gas	F		1.31?	19?	19.	
Chlorine	Gas	Cl	1.33	2.47	35.5	35.5	Scheele, 1774.
Bromine	Liquid	Br	2.96	5.54	80	80	Balard, 1826.
Iodine	Solid	I	4.95	8.79	127	127	Courtois, 1812.

115. These four elements compose a natural group, the members of which exhibit a gradation of similar properties. They are all found in minute quantities in sea water and in many mineral springs. They are frequently called the *halogens* (ἅλς, the sea), because they form binary compounds resembling seasalt; as, NaF, NaCl, NaBr, NaI. Such compounds are called the *haloid salts.* So, also, each of these elements combines with an equal volume of hydrogen to form an acid which is called a *haloid acid.* These acids are HF, hydrofluoric; HCl, hydrochloric; HBr, hydrobromic; HI,

hydriodic. The haloid acids are gases distinguished by a great attraction for water, and readily forming with it solutions which act as the free acids would act. In these compounds they are monads; but they seem also to act as triads, pentads, and even as septads. The halogens are never found native, and it is doubtful whether fluorine has ever been isolated.

The last three are liberated in the aëriform state by heating their haloid salts with a mixture of manganese dioxide and sulphuric acid. The general reaction may be expressed by the equation for chlorine:

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + 2\widehat{Cl}.$$

Their chemical energies are very active. The general order of their affinities for the positive elements is inversely as their atomic weights; their affinities for oxygen increase with their atomic weights. Fluorine is probably an incoercible gas; chlorine is a yellowish gas, liquefying at —40° C.; bromine, a red liquid, boiling at 63° C.; and iodine, a black solid, melting at 115° C. and boiling at 200° C.

Fluorine.

116. The most abundant compound of fluorine is fluor spar (CaF_2). It is also found in cryolite ($3NaF, AlF_3$), in many other minerals, and in the bones and the teeth.

117. The chemical properties of fluorine are probably analogous to those of chlorine. It forms no compounds with oxygen, nor with any others of the non-metals except hydrogen, boron, and silicon.

118. Hydrofluoric acid, HF. This acid is liberated in the gaseous state when powdered fluor spar is treated with twice its weight of strong sulphuric acid:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Anhydrous hydrofluoric acid is a colorless, volatile liquid which boils at 19.4° C., and emits dense fumes at ordinary temperatures. Both the gas and the liquid are readily soluble in water. The commercial acid of sp. gr. 1.15 has the formula $HF, 2H_2O$.

The acid powerfully corrodes the skin, a single drop producing a painful sore, and the fumes are dangerously irritating to the lungs. The most useful property which it possesses is its power of combining with silicon to form the gaseous fluoride of silicon (SiF_4). Glass is made of various silicates, as silicate of soda and silicate of lime; hence, hydrofluoric acid is used for etching glass.

Exp. 83.—Coat a glass plate with a thin layer of wax, and then, by means of a sharp point, engrave a word or drawing so that its lines shall expose the glass. Place the waxed surface over a leaden dish containing a mixture of fluor spar and sulphuric acid. Warm the dish gently, taking care not to melt the wax. In a few hours the glass will be etched by the gas. The liquid $HF, 2H_2O$ may also be used for etching glass. The white crust which generally forms when the glass is etched by gaseous HF is silica. This comes from the decomposition of the SiF_4 by the water which is obtained from the sulphuric acid.

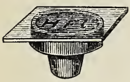


FIG. 35.

$$SiF_4 + 2H_2O = SiO_2 + 4HF.$$

119. The 4 HF thus liberated combines with a second portion of SiF_4 to form $2HF, SiF_4$, hydro-fluo-silicic acid, which does not corrode glass. Hydro-fluo-silicic acid forms difficultly soluble salts with potassium ($2KF, SiF_4$) and some other metals, and is sometimes used to separate these elements from their soluble compounds.

Exp. 84.—Mix 5 grammes of fluor spar with an equal quantity of powdered glass or clean sand. Put the mixture into a Florence flask furnished with a wide tube dipping into mercury in the receiver, and add 30 grammes of strong sulphuric acid. A gentle heat evolves

SiF_4. Now pour water above the mercury so carefully that none shall enter the tube. As the SiF_4 passes through the water it is decomposed, bubbles coated with an envelope of silica, SiO_2, form, and $2HF, SiF_4$ remains in solution. The silica may be filtered off through linen, and the solution of hydro-fluo-silicic acid preserved for future use.

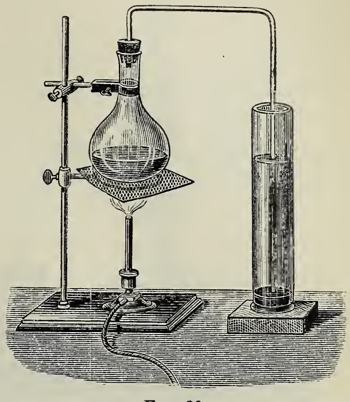


Fig. 36.

Chlorine.

120. Chlorine is a constituent of sodium chloride (common salt) and of potassium chloride, both of which are very abundant.

121. Preparation. Chlorine may be conveniently prepared by gently heating manganese dioxide with hydrochloric acid.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + \overset{\uparrow}{Cl_2}.$$

To obtain one litre of chlorine, about 20 grammes of the acid and 6 grammes of the dioxide are required.

The funnel tube shown in Fig. 37 answers for the introduction of the acid in small quantities, and also as a safety valve. Heat should not be applied until the oxide is thoroughly wetted by the acid. The gas may be washed by passing it through a small quantity of water in B. It is dried by passing it through strong sulphuric acid in C.

If the dry gas is wanted, it is collected by downward displacement, as represented in Fig. 37. The color of the gas easily shows when the jar is filled. The gas may then be kept for some time in the jar, if the stoppers are greased.

122. The gas can not be collected over cold water, because water at 10° C. absorbs 2.58 times its volume

of chlorine. It may, however, be collected over warm water or brine.

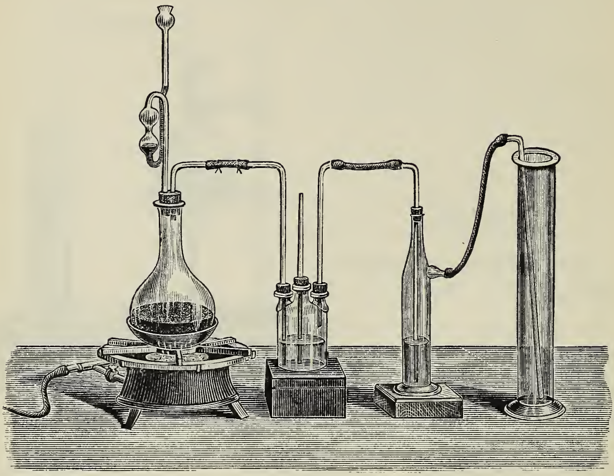


FIG. 37.

Exp. 85.—To prepare a solution of chlorine, or chlorine water, fill a retort with distilled water and place it in the position shown in Fig. 38. Carry a long delivery tube into the body of the retort, so that the chlorine may bubble through the water. Shake the retort from time to time, and keep it cool by pouring water on the outside. The operation may be stopped when the bubbles of gas are no longer absorbed.

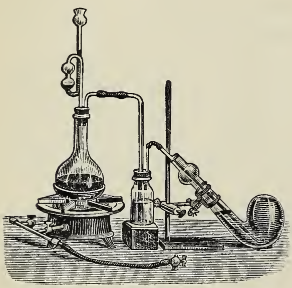


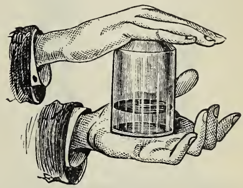
FIG. 38.

Chlorine water may be preserved for future use by storing it in bottles covered with black paper and kept in a cool place. It possesses most of the properties of the gas.

123. Physical properties. Chlorine is a greenish yellow gas of pungent odor. It is one of the heaviest

gases, being 2.47 times heavier than air. It may be condensed at 12.5° C. to a yellow liquid (sp. gr. 1.33), by a pressure of 8.5 atmospheres; but it has never been solidified, even at—90° C.

Exp. 86.—To show its rapid absorption by water, hold a jar of chlorine gas downward in water, and decant one-third of it. Now close the mouth of the bottle with the hand, and shake the bottle. The water will completely absorb the gas, producing a vacuum in the bottle, which will then be held to the hand by atmospheric pressure.



FIG, 39.

When saturated chlorine water is cooled to 0° C., yellow crystals of $Cl, 5H_2O$, chlorine hydrate, may be obtained. These crystals are used as a source for obtaining liquid chlorine.

124. The chemical properties of chlorine are very active, and give rise to the various phenomena of combination, displacement and substitution, and indirect oxidation.

125. (I) **Combination.** Very nearly all the elements unite directly with chlorine. O. C. F. are exceptions.

Exp. 87.—Prepare several jars of the dry gas. Powdered antimony sprinkled into the chlorine forms $SbCl_5$, generally evolving flashes of light. A similar result follows by using powdered metallic arsenic or bismuth.

Exp. 88.—Place in a deflagrating spoon a piece of dry phosphorus, and plunge this into a jar of the gas. The two elements combine with a pale flame to form PCl_3 or PCl_5. (See Fig. 29.)

Exp. 89.—Stir gold leaf in chlorine water. It soon dissolves to $AuCl_3$.

126. (II) **Displacement and substitution.** The most

important applications of chlorine depend on its affinity for hydrogen.

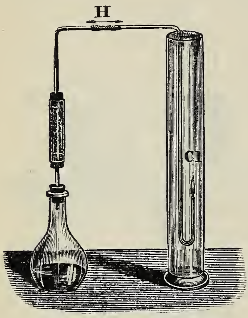


FIG. 40.

If a jet of burning hydrogen be introduced into a jar of chlorine, it will continue to burn with the formation of HCl. A mixture of the two gases combines slowly in diffused light, but suddenly and with explosive force in the direct sunlight. (See Exp. 56).

Exp. 90.—Pour chlorine water into a solution of hydrogen sulphide. The latter is decomposed with precipitation of sulphur, and hydrochloric acid is formed. $H_2S + 2\,Cl = 2\,HCl + S$.

Exp. 91.—To a tube two-thirds full of chlorine water add enough ammonia solution to fill it; then invert the tube in a capsule of water. Bubbles of nitrogen will rise to the top, and hydrochloric acid will be formed: $NH_3 + 3\,Cl = 3\,HCl + N$. The hydrochloric acid will then combine with another portion of the ammonia to form NH_3HCl, ammonium chloride.*

Exp. 92.—Wet strips of filter paper with *warm* turpentine, and plunge into a jar of dry chlorine. The turpentine will be decomposed; its hydrogen will unite with chlorine, and dense fumes of carbon will be evolved, as carbon does not unite directly with chlorine. (Fig. 41).

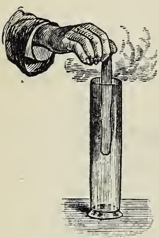


FIG. 41.

Hence, if lighted tapers be plunged into chlorine gas, they burn feebly with a smoky flame, only the hydrogen of the taper combining with the chlorine. (Fig. 42).

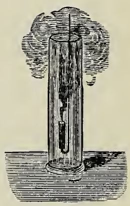


FIG. 42.

So, also, chlorine will decompose water. If a tube filled with chlorine water be inverted in water and placed in the sunlight, bubbles of oxygen will collect at the top of the tube. The hydro-

* Care must be taken to keep the ammonia in excess; otherwise, a very explosive compound, nitrogen chloride ($NHCl_2$, NCl_3), will also be formed.

chloric acid formed dissolves in the excess of water. (See Exps. 7 and 28): $H_2O + 2\,Cl = 2\,HCl + \overset{\frown}{O}$.

127. (III) **Indirect oxidation.** The last experiment shows that chlorine may be used as an oxidizing agent. When so used, the oxygen liberated is applied in the nascent state and is very energetic.

Exp. 93.—Add to a solution of manganous sulphate a little potassium hydrate: white manganous oxide precipitates. Now add a few drops of chlorine water: black dioxide of manganese immediately forms; $MnO, H_2O + 2\,Cl = MnO_2 + 2\,HCl$,

128. Uses. (I) *Bleaching properties.* Dye stuffs are frequently organic compounds containing hydrogen. If chlorine acts upon such dyes in the presence of water, they are changed to colorless compounds as the result of chlorination or of oxidation. Hence, chlorine is an excellent bleaching agent.

Exp. 94.—Place strips of printed calico in chlorine water, or expose them in a damp state to the action of the gas. Most of the colors will soon disappear. Indigo first oxidizes to isatin, and then changes to chlorisatin, both of which are soluble in water and are nearly colorless.*

The experiment may be repeated with green leaves or flowers. Most mineral colors remain unaltered. Printers' ink is not affected at all, as it is largely carbon.

(II) *Disinfecting properties.* Among the noxious products of the decay of animal and vegetable matters are ammonia, hydrogen sulphide, and similar compounds. Chlorine acts upon these compounds in the same way that it acts upon coloring matters, and converts them into harmless substances. Hence it is of great value as a disinfectant.

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* C_8H_5NO (indigo) $+ H_2O + Cl_2 = C_8H_5NO_2$ (isatin) $+ 2\,HCl$.
$C_8H_5NO_2$ (isatin) $+ Cl_2 = C_8H_4ClNO_2$ (chlorisatin) $+ HCl$.

TESTS.—Free chlorine may be recognized, (1) by its odor, (2) by its bleaching properties, and (3) by its producing a blue color in acting upon a mixture of starch and potassium iodide (Exp. 28).

129. Hydrochloric acid, HCl. Discovered by Priestley.

Preparation. — Introduce about 20 grammes of fused sodium chloride into a flask, and pour over it 40 grammes of sulphuric acid. Heat the flask very gently, and collect the gas by displacement in dry jars.*

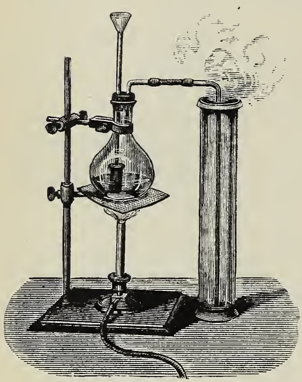


FIG. 43.

130. Physical properties. Hydrochloric acid is a colorless gas, having an acid taste and pungent odor. It has a specific gravity of 1.27, and may be condensed by a pressure of 40 atmospheres to a colorless liquid. At 15° C., one volume of water absorbs 400 times its volume of the gas.

Exp. 95.—Its solubility in water may be shown by fitting to a bottle containing the gas a cork furnished with a glass tube, and inverting the bottle over water. In a short time the water will rush into the bottle as if into a vacuum.

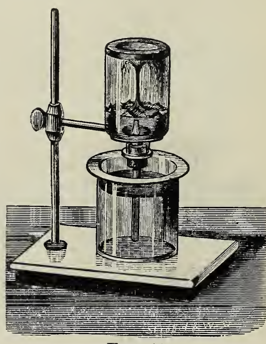


FIG. 44.

The commercial acid, frequently called muriatic acid, is made by passing the gas into a series of bottles containing cold water. (Fig. 45). When this acid has a specific gravity of 1.21, it contains 43 per cent, by weight, of HCl, and may be represented by the formula, $HCl + 3H_2O$.

* $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

131. Chemical properties. Hydrochloric acid dissolves many metals and their oxides, forming with them chlorides which are represented by KCl, $FeCl_2$, and Fe_2Cl_6. All of the metallic chlorides are soluble in water except AgCl, Hg_2Cl_2, $PbCl_2$, TlCl, and Cu_2Cl_2. When hydrochloric acid acts upon an oxide, two atoms of chlorine are required to displace one atom of oxygen. Thus:

$$FeO + 2HCl = FeCl_2 + H_2O.$$
$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$

When no chloride so corresponding to the oxide exists, part of the chlorine is set free and a lower chloride formed. This is generally the case with the peroxides; as, MnO_2, PbO_2; $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$.

TESTS.—HCl gas forms, with the vapor of ammonia, white fumes of NH_3, HCl. Solutions of HCl, or of the metallic chlorides, yield, with silver nitrate, a white, curdy precipitate, AgCl, soluble in ammonia, but insoluble in nitric acid.

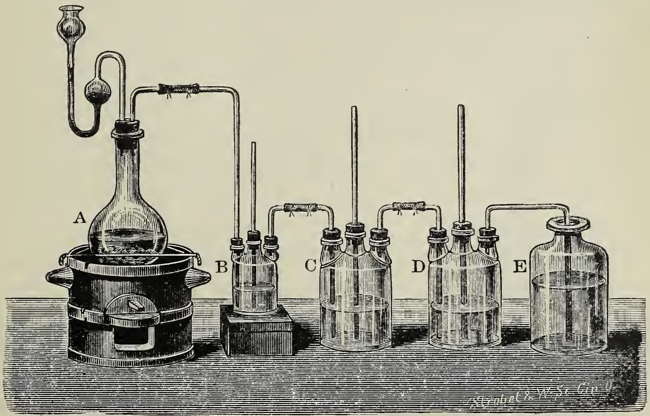


FIG. 45.

132. Uses. Enormous quantities of hydrochloric acid are evolved in the manufacture of soda. This acid is used as a source of chlorine in the manufacture of cal-

cium hypochlorite. In the laboratory it finds constant employment as a convenient solvent.

133. The compounds of chlorine and oxygen. Chlorine forms the following series of acids, which may be regarded as formed from an anhydride, with the addition of one molecule of water, or as oxides of hydrochloric acid.

WATER.	ANHYDRIDE.	NAME OF ACID.	HCl.
H_2O, +	Cl_2O	= hypochlorous acid,	$2 \times HClO$.
H_2O, +	Cl_2O_3	= chlorous acid,	$2 \times HClO_2$.
H_2O, +	Cl_2O_5	= chloric acid,	$2 \times HClO_3$.
H_2O, +	Cl_2O_7	= perchloric acid,	$2 \times HClO_4$.

Only the first two anhydrides have been isolated. The acids are seldom prepared. They are very unstable, and are liable to produce dangerously explosive compounds. Besides these, there exists chloric peroxide, Cl_2O_4, for which no corresponding acid is known.

134. Hypochlorites. The best known hypochlorites are sold under the names of "chloride of lime" and "chloride of soda." These are mixtures which owe their useful properties to the calcium hypochlorite, CaO, Cl_2O, and sodium hypochlorite, Na_2O, Cl_2O, which they contain. They are excellent bleaching and disinfecting agents. Hypochlorous acid is itself more energetic than chlorine, probably because, on breaking up, it evolves chlorine and oxygen, both in their nascent state.

We may study its properties by means of a solution prepared from good "chloride of lime."

Exp. 96.—Add to a little of the solution an equal amount of dilute nitric acid. Yellow fumes will be given off, which are hypochlorous acid.

Exp. 97.—Repeat the experiment, using an excess of sulphuric or hydrochloric acid. Only chlorine will be liberated.

Exp. 98.—Place in each of the preceding mixtures, and also in a fresh quantity, paper which has been written upon, and notice the relative rapidity with which each is bleached.

Exp. 99.—Add a few drops of the solution to a solution of manganous chloride or of cobaltous nitrate; the black precipitates which fall are MnO_2 or Co_2O_3. The protoxides have acquired additional oxygen from the calcium hypochlorite.

Exp. 100.—Add a few drops of cobaltous nitrate to a pint of the solution, and heat. A large quantity of oxygen will be given off, which may be collected and tested. The cobaltic oxide seems to act as a carrier of the oxygen, first combining with it and then giving it off.

135. The hypochlorites are prepared by passing chlorine through or over the metallic hydrates.

Exp. 101.—Pass a slow current of chlorine gas into a cold dilute solution of potassium hydrate. The solution acquires strong bleaching properties from the formation of potassium hypochlorite.

$$2\,(K_2O, H_2O) + 4\,Cl = K_2O, Cl_2O + 2\,KCl + 2\,H_2O.$$

136. The chlorates. If this solution be boiled, it will be converted into potassium chloride and potassium chlorate: $3\,(K_2O, Cl_2O) = 4KCl + K_2O, Cl_2O_5$ or $2\,(KClO_3)$.

Exp. 102.—Pass a rapid stream of chlorine gas into a moderately strong solution of potassium hydrate. The liquid will soon become hot enough to decompose the hypochlorite, and the ultimate result will be thus expressed:

$$6\,K_2O, H_2O + 12\,Cl = K_2O, Cl_2O_5 + 10\,KCl + 6\,H_2O.$$

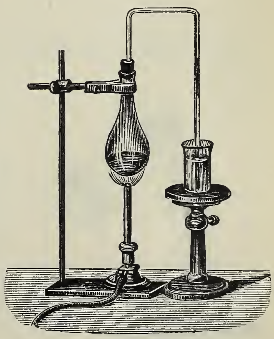


FIG. 46.

If the solution be allowed to cool, tabular crystals of potassium chlorate will be deposited. If the solution be then poured off, and the crystals redissolved in boiling water, a second crop of crystals may be obtained, which are nearly pure potassium chlorate.

137. Chloric acid, H_2O, Cl_2O_5 or $HClO_3$. If a solution of potassium chlorate be mixed with hydro-fluo-silicic

acid, potassium silico-fluoride is deposited, and hydrated chloric acid remains in the solution.

$$K_2O, Cl_2O_5 + 2HF, SiF_4 = 2KF, SiF_4 + H_2O, Cl_2O_5.$$

This solution concentrated *in vacuo* yields a syrupy, yellow liquid of peculiar odor. It inflames paper, sulphur, and phosphorus — sometimes with explosive violence. The acid and its salts are easily decomposed by heat and by the stronger acids, and are among the most energetic oxidizing agents known.

Exp. 103.—Powder *separately* equal weights of sugar and potassium chlorate, and then mix the powders carefully. The mixture, touched with a glass rod dipped in sulphuric acid, burns with a brilliant white light.

Exp. 104.—A little of the sugar mixture, wrapped in paper and struck by a hammer, detonates violently. If half of the sugar is replaced by dried potassium ferro-cyanide, it forms "white gunpowder."

Exp. 105.—Potassium chlorate forms with sulphur or phosphorus detonating compounds. If a *very little sulphur* be rubbed in a mortar with potassium chlorate, frequent explosions will take place.

138. Chloric peroxide and chlorous acid are dangerous to prepare on account of their explosive character.

Fig. 47.

Exp. 106.—Drop a few crystals of potassium chlorate into a glass of water containing a few small slices of phosphorus. Now, by means of a pipette, add a little sulphuric acid to the bottom of the glass. A yellow gas, chloric peroxide (Cl_2O_4 or ClO_2), is formed, and oxidizes the phosphorus with bright flashes of light and slight detonations.

Exp. 107.—Add a few crystals of potassium chlorate to hydrochloric acid, and warm gently if no action immediately ensues. A yellow gas called *euchlorine* is evolved. It has very energetic

bleaching and oxidizing properties, and is probably a mixture of chlorine with anhydrous chlorous and chloric acids.

139. Potassium perchlorate is formed when potassium chlorate is gently heated until the mass becomes pasty. One-third of the oxygen is given off, and the remainder is a mixture of potassium chloride and potassium perchlorate: $2(K_2O, Cl_2O_5) = K_2O, Cl_2O_7 + 2KCl + O_4$. If this mass is dissolved in hot water, and the solution allowed to cool, potassium perchlorate crystallizes out. Perchloric acid may be obtained from this salt by precipitating the potassium by hydro-fluo-silicic acid (§**137**).

The perchlorates do not yield Cl_2O_4 when treated with sulphuric acid. They have no commercial uses.

Tests.—These experiments are also tests for the compounds of oxygen and chlorine. When heated, they are all converted to chlorides, and may then be tested as such.

Bromine.

140. Bromine occurs in the waters of many saline springs and in sea water. When such liquids are evaporated, most of the other salts crystallize out, and the liquid remaining ("bittern") contains magnesium and sodium bromides.*

Fig. 48.

141. Preparation. These liquids are treated with chlorine, the bromine is set free, and the vapors which escape are collected in a cooled receiver. These consist of liquid bromine and an aqueous solution of bromine.

Exp. 108.—Add chlorine water to a solution of potassium bromide. Bromine will separate out and render the liquid yellowish red. Place this liquid in a separatory funnel (Fig. 48), and add a little ether. Shake the mixture and then allow it to stand. An ethereal solution of bromine will rise to the top.

142. Physical properties. At 15° C., bromine is a

* Nearly 200,000 pounds of bromine are made in Ohio annually.

dark red liquid of a disagreeable odor, from which it derives its name (βρῶμος, a stench): sp. gr. 2.96. It solidifies at —22°, boils at 63° C., and yields abundant vapors at ordinary temperatures. It is sparingly soluble in water; readily in ether and in carbonic disulphide.

143. Its chemical properties are like those of chlorine. It has a strong affinity for hydrogen, and, therefore, may be used as an agent for indirect oxidation, for bleaching, and for disinfecting.

Exp. 109.—Vaporize a few drops of bromine in a jar, and introduce a pellet of dry phosphorus. PBr_3 is formed, with evolution of light.

With other jars test its bleaching properties, etc., as with Cl.

Tests.—Free bromine is recognized by its odor, and by the orange color it gives to a starch solution.

The bromides give, with silver nitrate, yellowish white silver bromide, AgBr, which is converted by chlorine water into AgCl and free Br. The Br may be separated by shaking with ether.

144. Uses. The bromides are used in photography and in medicine. Free bromine is used in some chemical operations in preference to chlorine.

Bromine forms HBr (hydrobromic acid), H_2O, Br_2O (hypobromous acid), and H_2O, Br_2O_5 (bromic acid), which resemble the corresponding chlorine compounds.

Iodine.

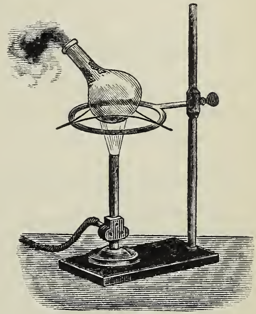
145. Iodine is contained in sea water in exceedingly minute quantities. Certain marine plants and animals contain it in such proportions that it can be obtained from their ashes with profit.

146. Preparation. The ashes of sea weed, called *kelp*, are treated with a little hot water, and the solution which forms is set aside to crystallize. The mother

liquors contain sodium iodide, NaI. These liquors, heated with manganese dioxide and sulphuric acid, evolve free iodine, which is collected in cooled receivers. The iodine may also be isolated by chlorine. (Exps. 19 and 28).

147. Physical properties. Iodine is a grayish black, crystalline solid. It volatilizes at ordinary temperatures, melts at 115° C., and boils at 200° C., evolving the beautiful vapors from which it derives its name (*ἰώδης*, violet-colored).

It dissolves in 7,000 parts of water; readily in aqueous solutions of metallic iodides, in alcohol, ether, and chloroform. Its best solvent is carbonic disulphide.



FIG, 49.

Exp. 110. — (1) Volatilize a grain of iodine in a dry flask: (2) after the sublimate has cooled, dissolve it in a few drops of alcohol: (3) add water, and most of the iodine will precipitate: (4) shake a little of the aqueous solution in a test tube with ten drops of carbonic disulphide. On standing, the disulphide will settle to the bottom of the tube, and its color change to violet, owing to the dissolved iodine.

148. The chemical properties of iodine are less energetic than those of chlorine and bromine. Either of these elements displaces it from its haloid salts. Its bleaching powers are very feeble. We have already seen that it unites directly with other elements. (Exps. 10, 11, 12, 15). It acts corrosively upon organic tissues, staining the skin yellow.

TESTS.—Free iodine forms a beautiful blue color with starch paste, and a violet solution with CS_2.

The iodides give, with silver nitrate, a buff-colored AgI; with mercuric chloride, scarlet HgI_2. Any iodide treated with chlorine

yields free iodine, which may then be tested with starch paste. An excess of chlorine should be avoided.

The iodine may also be set free by potassium nitrite acidulated with acetic acid.

149. Uses. Iodine is largely used in the manufacture of aniline green and in photography. The element and its salts are employed in medicine, especially for the treatment of enlarged glands.

150. Hydriodic acid, HI. Free hydrogen and iodine do not readily unite; but, when iodine is present with nascent hydrogen, the two elements unite to form hydriodic acid.

This is illustrated by Exp. 31. Nevertheless, hydriodic acid is a very unstable body. It is readily decomposed by the oxygen of the air, forming water and depositing iodine. It may even act as a reducing agent. In the experiment just cited, it is necessary that the solution of sulphurous acid be very dilute, for, otherwise, considerable sulphuric acid is formed, and is again reduced by the hydriodic acid to sulphurous acid.

$$H_2SO_4 + 2\,HI = H_2SO_3 + H_2O + 2\,I.$$

A solution of hydriodic acid is conveniently prepared by passing hydrogen sulphide through water containing iodine in suspension: $H_2S + 2\,I = S + 2\,HI$. The separated sulphur is filtered off, and the solution warmed to expel the excess of hydrogen sulphide.

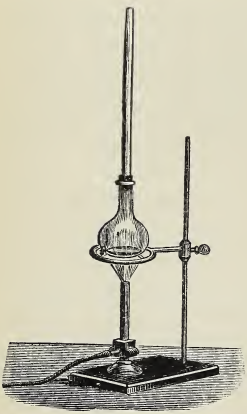


Fig. 50.

151. Oxides of iodine. Iodine has a much stronger affinity for oxygen than either chlorine or bromine. Iodic acid, H_2O, I_2O_5, may be obtained by heating iodine with strong nitric acid in a flask, to which is fitted a long glass tube that serves to condense the iodine which volatilizes unchanged. By heating this to 170° C., iodic anhydride,

I_2O_5, may be obtained. At about 370° it is decomposed. The acid forms iodates which closely resemble their corresponding chlorates.

There exist, also, periodic acid, H_2O, I_2O_7, and other compounds whose composition has not been determined with certainty.

Recapitulation.

The halogens are volatile elements which usually act as electro-negative monads.

Fluorine is characterized by a wonderful affinity for silicon.

Cl, Br, and I form a natural group whose relations to each other are more intimate than are those of any one of them to F.

All combine readily with hydrogen, forming acids which are exceedingly soluble in water. Cl decomposes water rapidly in the sunlight. Br slowly, and I not at all.

By reason of this affinity for hydrogen, Cl and Br, in the presence of H_2O, act indirectly as oxidizing, bleaching, and disinfecting agents. HI is easily decomposed, and is an important reagent in organic chemistry as a source of nascent iodine.

All combine directly with most metals to form haloid salts. The most common in nature are those containing Na, K, Ca, or Al.

The haloid salts are frequently associated together in nature, and are generally isomorphous.

They tend to form double salts, as $2\,KI, HgI_2$. This is especially characteristic of the salts of fluorine, as $2\,KF, SiF_4$.

Fluorine forms no compounds with oxygen.

The oxy-salts of the others are easily decomposed, yielding the haloid salt and free oxygen. Hence, the oxy-salts may be used, either alone or with strong acids, as oxidizing agents.

CHAPTER VI.

THE SULPHUR GROUP.

ELEMENT.	SYMBOL.	SPECIFIC GRAVITY. SOLID. $H_2O = 1$.	SPECIFIC GRAVITY. VAPORS. AIR = 1.	ATOMIC WEIGHT.	FUSING POINT.	DISCOVERER.
Sulphur	S	2.05	2.21	32.	120°	
Selenium	Se	4.79	5.48	79.5	250°	Berzelius, 1817.
Tellurium	Te	6.65	8.91	129.	500°	Klaproth, 1798.
Oxygen	O		1.106	16.		Priestley, 1774.

152. A natural gradation of properties is also exhibited by this group. Their specific gravities, melting points, and atomic weights form an increasing series. Their chemical energies are in a reverse order, sulphur being the most active and tellurium the least.

They are each characterized by forming fetid aëriform compounds containing two volumes of hydrogen to one of the other element—the three volumes condensing to two; as, H_2S, H_2Se. In this respect, oxygen is allied to this group, as also in the fact that each of them is capable of replacing oxygen in most of its compounds, atom for atom. Hence, they are generally ranked among the dyad elements; but they also form compounds in which they are quadrivalent, as SCl_4, and sexivalent, as $S(C_2H_4)''(C_2H_5)'_2 Br'_2$. Their highest atomicity, therefore, classes them as negative hexads.

153. Each element of this group forms two acid anhydrides with oxygen, and at least two acids, which have similar formulæ and properties.

Type, H_2O	Type, $2H_2O$ or $\begin{matrix}H_2\\H_2\end{matrix}>O_2$			
	ANHYDRIDES	"OUS" ACIDS	ANHYDRIDES	"IC" ACIDS
H_2S	SO_2	H_2O, SO_2 or H_2SO_3	SO_3	H_2O, SO_3 or H_2SO_4
H_2Se	SeO_2	H_2O, SeO_2 or H_2SeO_3	SeO_3*	H_2O, SeO_3 or H_2SeO_4
H_2Te	TeO_2	H_2O, TeO_2 or H_2TeO_3	TeO_3	H_2O, TeO_3 or H_2TeO_4

The hydrogen of each of these compounds is replaceable by two atoms of a monad metal or by one atom of a dyad, to form corresponding salts; as, K_2S, K_2SO_4, CaS, $CaSO_4$.

154. The physical properties of tellurium ally this group to the metals. It conducts heat and electricity, though not readily, and has a brilliant metallic luster. Sulphur is a non-conductor of heat and of electricity, and has a vitreous luster. Selenium, a red solid, is midway between them. Finally, all three occur native,—selenium frequently associated with sulphur, tellurium associated with gold and other metals.

NOTE.—Lately an ore of gold has been found in Colorado combined with considerable quantities of tellurium; but tellurium and selenium are still so rare as to need no further description.

SULPHUR.

155. Sulphur is found native in considerable quantities. It occurs in many minerals as sulphides—*e. g.*, iron pyrites (FeS_2), copper pyrites (Cu_2S, FeS_2), galena (PbS), blende (ZnS), cinnabar (HgS); and as sulphates—*e. g.*, gypsum ($CaSO_4$), heavy spar ($BaSO_4$), Epsom salts ($MgSO_4$), and Glauber's salts (Na_2SO_4). It is also a constituent of many organic products, as casein, fibrin, albumin, and the oils of cruciferous and alliaceous plants, as mustard and garlic.

* Selenic anhydride has not been isolated.

156. Preparation. In order to free it from its earthy impurities, native sulphur generally requires to be distilled.

The vapors are conducted into large brick chambers, and are there condensed. The flowers of sulphur are the first product obtained while the walls of the chamber are yet cold. After a time, the walls of the chamber become heated; the sulphur melts and is cast into wooden moulds to form roll sulphur or brimstone.

157. Physical properties. Sulphur is a brittle, yellow solid, tasteless and almost inodorous. On being heated, it becomes a limpid fluid at 120° C.: as the temperature rises, it darkens and thickens, until, at about 250° C., it is so viscid that the vessel in which it is contained may be inverted without spilling it: above 300° C. it again liquefies, boils at 440° C., and is converted into an orange vapor, which, at 500° C., has a density of 96, and at 1000° C., the normal density of 32.

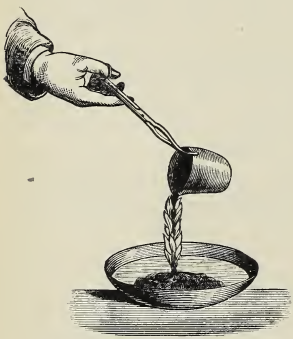


FIG. 51.

If, now, the vessel is removed from the flame, and a small quantity is poured into cold water, it forms an amorphous, elastic mass called *plastic sulphur*. The portion remaining in the vessel passes, as it cools, through the viscid and limpid states, and finally crystallizes in oblique prisms. If the liquid portion be poured off as soon as a crust has formed on the surface, the crystals will be found lining the interior walls.

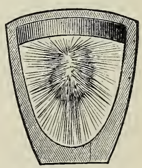


FIG. 52.

If, now, some of the crystals are dissolved in carbonic disulphide, and the solution is allowed to evaporate spontaneously, beautiful octahedral crystals are deposited, resembling those of native sulphur.

Plastic sulphur is not soluble in carbonic disulphide.

158. Sulphur has, then, at least three allotropic states: (1) the octahedral, (2) the oblique prismatic, and (3) the plastic. The milk of sulphur is another modification, obtained by precipitating sulphur from the alkaline poly-sulphides by the addition of acids. All of these are changed to the prismatic form by fusion, and all, on standing, assume more or less perfectly the octahedral condition.

Exp. 111.—Confirm these facts by performing the operations indicated. A test tube will suffice to show the changes assumed by heating; but, to obtain fine oblique prisms, a good-sized crucible is required.

159. Chemical properties. Sulphur enters into direct combination with many of the elements.

Exp. 112.—Heat in a test tube a mixture of sulphur with twice its weight of copper filings. The two elements unite with vivid combustion at a temperature a little above the melting point of sulphur. (See also Exp. 14).

The compounds with the metals are sulphides. These have, in general, properties and formulæ analogous to their corresponding oxides, as FeS, CuS.

Carbonic disulphide, CS_2, is formed by passing the vapor of sulphur over ignited coals. (See § 305).

Sulphur heated in the air inflames at 250° C., and burns with a pale blue flame, being converted into sulphurous anhydride, SO_2, and evolving peculiar, suffocating fumes, the same as are noticed in burning matches coated with sulphur.

160. Tests. Free sulphur is recognized by its physical properties and by its peculiar odor when burned.

Sulphur in combination may be detected by (1) placing in a small tube of very thin glass a little magnesium or sodium: (2) covering the metal with the substance to be tested, which must be perfectly free from water; and (3) then heating the mixture in the flame of a lamp. A vivid combustion ensues, and a sulphide (hepar) is formed. (4) On bringing this sulphide upon a bright

silver coin, and moistening the mass with water, a black stain (Ag_2S) will be produced on the silver if sulphur is present.

The hepar may also be made by fusing a substance which contains sulphur upon coal, with sodium carbonate, before a flame free from sulphur.

161. Uses. Large quantities of sulphur are used in preparing its numerous compounds, as sulphuric acid, etc., in vulcanizing India rubber, and in making matches and gunpowder.

162. Hydrogen sulphide, also called sulphuretted hydrogen and hydrosulphuric acid, H_2S, occurs native in "sulphur springs," and is one of the causes of the odors of putrefying organic substances, as of rotten eggs.

163. Preparation. Hydrogen sulphide is generally prepared by decomposing ferrous sulphide with dilute sulphuric acid: $FeS + H_2O, SO_3 = FeO, SO_3 + H_2S$.

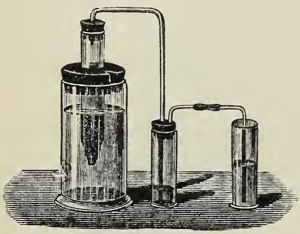


FIG. 53.

The process is similar to that described in Exp. 23. Fig. 53 exhibits an apparatus which is convenient when small quantities of the gas are wanted from time to time. A bit of glass tubing, made funnel-shaped at one end, contains the ferrous sulphide. It is supported by a cleft cork in the large cylinder, which contains the dilute acid. When the tube is pushed down into the cylinder, the acid enters through the mouth of the funnel, and the reaction begins. It may be stopped by lifting the tube out of the acid. The smaller cylinder contains a little water, in order to wash the gas.

164. Physical properties. Hydrogen sulphide is a colorless, coercible gas of extremely offensive odor: sp. gr. 1.178. At ordinary temperatures, water absorbs about three times its volume of the gas.

165. Chemical properties. The gas is readily inflammable, and burns with a blue flame like that of sulphur. Its solution is readily decomposed by chlorine, bromine, or iodine, by many oxidizing agents, and even by prolonged contact with the air. In such cases the sulphur is generally deposited, and the hydrogen unites with the chlorine, oxygen, etc. Hence, it may act as a reducing agent.

Exp. 113.—Add a few drops of calcium hypochlorite to a solution of hydrogen sulphide. The "milk of sulphur" is deposited.

$$CaCl_2O_2 + 2\,H_2S = CaCl_2 + 2\,H_2O + \underline{S_2}.$$

Exp. 114.—Acidulate a solution of potassium bichromate with sulphuric acid, and then add hydrogen sulphide. On warming the solution a green color appears, which indicates the production of chromic sesquioxide:

$$K_2O, 2\,CrO_3 + 4\,H_2O, SO_3 + 3\,H_2S = K_2O, SO_3 + Cr_2O_3, 3\,SO_3 + 7\,H_2O + 3\,\underline{S}.$$

Chromic anhydride is reduced to chromic sesquioxide, and ferric salts to ferrous salts:

$$2\,CrO_3 + 3\,H_2S = Cr_2O_3 + 3\,H_2O + \underline{S_3};$$
$$Fe_2Cl_6 + H_2S = 2\,FeCl_2 + 2\,HCl + \underline{S}.$$

166. Uses. Besides this reducing action, it is largely employed in the laboratory as a group reagent.

I. It precipitates from their solutions Hg, Pb, Ag, Cu, Cd, Bi, as sulphides, insoluble in dilute acids or in alkaline sulphides.

II. It precipitates from solutions feebly acid As, Sb, Sn, Au, Pt, as sulphides, which act as sulpho-acids, and combine with the alkaline sulphides to form sulpho-salts that are soluble in water. Hence, these elements are not precipitated in alkaline solutions.

III. The sulphides of Ni, Co, Fe, Mn, Zn, U, are soluble in dilute acids; hence, they are precipitated only in alkaline solutions or by alkaline sulphides.

IV. Aluminium and chromium do not form sulphides in the wet way, but are precipitated as oxides by the alkalies in presence of hydrogen sulphide.

V. The sulphides of the more electro-positive elements, as Mg, K, are easily soluble in water, and, hence, are not precipitated by H_2S.

Exp. 115.—Arrange five test glasses to represent these groups. Pour a solution of arsenious acid into I, of lead nitrate into II, ferric chloride into III, alum into IV, potassium hydrate into V, and pass a current of the gas into each of these. Yellow As_2S_3 will form in I; black PbS, in II; white S, in III, from a reduction of Fe_2Cl_6 to $FeCl_2$; and no apparent reaction will take place in the others. Now add a little of V to the As_2S_3—it redissolves; to the PbS—it is unchanged; to a fresh solution of ferric chloride—black FeS precipitates; to alum—white $Al_2O_3, 3H_2O$ falls. Add ammonia to III and IV: the same change occurs as in the last two examples.

I II III IV V

Fig. 54.

Tests.—Hydrogen sulphide may be recognized by its odor and by its reactions upon members of group I. Strips of "lead paper," made by dipping unsized paper into a solution of lead acetate, are very useful for this purpose. The alkaline sulphides strike a purple color with sodium nitro-ferro-cyanide, even in very dilute solutions.

167. Physiological properties. The gas is exceedingly poisonous when breathed, and, even when much diluted, it gives rise to nausea and vertigo.

168. The compounds of sulphur and oxygen. Two anhydrides of sulphur have been isolated—sulphurous anhydride, SO_2, and sulphuric anhydride, SO_3. They each combine with one molecule of water to form sulphurous acid, H_2O, SO_2, and sulphuric acid, H_2O, SO_3. These are of great use in the arts. There exists, also, a series of acid compounds containing more than one atom of sulphur, which are known collectively as the polythionic series (*θειον*, sulphur). Of this series, only the thiosulphates are of commercial importance.

The acid compounds may be arranged as follows. Several formulæ are given of each, to illustrate different methods of notation.

I. MONOTHIONIC SERIES.

$$O{=}S{<}^{H}_{OH} \text{ or } H'(SO)''(OH)' \text{ or } H_2O, SO(?) \text{ or } H_2SO_2.$$

Hydrosulphurous or hyposulphurous acid.*

$$O{=}S{<}^{OH}_{OH} \text{ or } (SO)''(OH)'_2 \text{ or } H_2O, SO_2 \text{ or } H_2SO_3.$$

Sulphurous acid.

$$^{O}_{O}{\gtrdot}S{<}^{OH}_{OH} \text{ or } (SO_2)''(OH)'_2 \text{ or } H_2O, SO_3 \text{ or } H_2SO_4$$

Sulphuric acid.

II. POLYTHIONIC SERIES.

$$^{O}_{O}{\gtrdot}S{<}^{SH}_{OH} \text{ or } (HS)'(SO_2)''(OH)' \text{ or } H_2O, S_2O_2 \text{ or } H_2S_2O_3.$$

Hyposulphurous or thiosulphuric acid.*

III.

$SO_2{-}OH$ $\vert$ $SO_2{-}OH$	$S{<}^{SO_2-OH}_{SO_2-OH}$	$S{-}SO_2{-}OH$ $\vert$ $S{-}SO_2{-}OH$	$S{<}^{S-SO_2-OH}_{S-SO_2-OH}$
or	or	or	or
$H_2S_2O_6$	$H_2S_3O_6$	$H_2S_4O_6$	$H_2S_5O_6$
Dithionic acid.	Trithionic acid.	Tetrathionic acid.	Pentathionic acid.

169. All these acids are dibasic; that is, their hydrogen may be exchanged for one dyad or for two monad atoms. If both hydrogen atoms are thus replaced, the salt is normal, as K_2SO_4, potassium sulphate; if only one hydrogen atom is replaced by a monad, the salt is acid, as $KHSO_4$, acid potassium sulphate, or bisulphate of potassa. If two different metals take the place of the hydrogen, the resulting salt is double, as $K'_2Cu''(SO_4)_2 + 6H_2O$.

170. Sulphurous anhydride, SO_2, is found in nature among the gases issuing from volcanoes. No considera-

*A lamentable confusion exists in the names of the first and fourth. By strict analogy, salts of the first should be called hyposulphites, as Na_2SO_2; but long use has given salts of the fourth acid; as $Na_2S_2O_3$, the name hyposulphites, and it is difficult to change a name which has become familiar. They should be called thiosulphates.

ble quantity is found in the air of towns, although it must be continually evolved in the burning of coals which contain sulphur.

171. Preparation. Sulphurous anhydride is the sole product of the combustion of sulphur in oxygen. It is generally prepared for laboratory purposes by heating strong sulphuric acid with either mercury or copper.

$$2(H_2O, SO_3) + Cu = CuO, SO_3 + 2H_2O + \overset{\frown}{SO_2}.$$

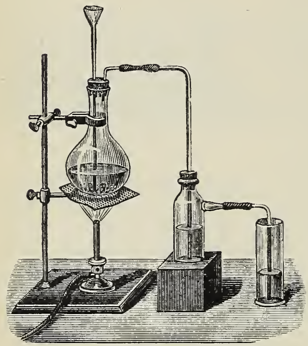


Fig. 55.

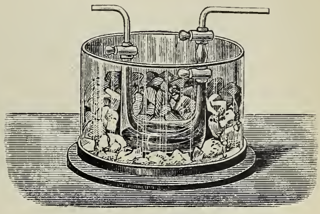
Exp. 116.—Heat in a flask 20 grammes of copper clippings with 60 cc. (Fig. 35) of strong sulphuric acid. Collect a portion of the gas by displacement in dry cylinders, and then form a solution of the gas by passing it into water. (Fig. 55). When the operation is finished and the flask is cooled, there will be found a grayish powder at the bottom of a brown liquid. Decant the liquid, add a little water to the powder, boil, and filter. After a little while, crystals of blue cupric sulphate will be formed in the filtrate. Often there remains on the filter a dark powder which is insoluble in water: this is a sulphide of copper, formed by the complete reduction of the sulphuric acid.

$$(a)\ H_2O, SO_3 + 4\,Cu = CuS + H_2O + 3\,CuO.$$
$$(b)\ 3\,CuO + 3\,(H_2O, SO_3) = 3\,(CuO, SO_3) + 3\,H_2O.$$

172. Physical properties. Sulphurous anhydride is a colorless, easily coercible gas of a pungent, suffocating odor: sp. gr. 2.25. It condenses, at —10° C., to a colorless fluid, which solidifies at —79° C: sp. gr. 1.49.

Exp. 117.—Pass the gas from the flask in which it is generated, (1) into an empty bottle surrounded by ice, in order to cool it; then (2) through a chloride of calcium tube, to dry it; and (3) into a U tube surrounded by a mixture of ice and salt. (Fig. 56).

Sulphurous anhydride condenses, and may be preserved in sealed tubes or in soda water bottles.



Fig, 56.

Liquid sulphurous anhydride produces, by its evaporation, cold so intense as sometimes even to freeze itself. It freezes water readily,* and mercury if the evaporation is assisted by a brisk current of air.

Water at 15° C. absorbs 45 times its volume of the gas, forming sulphurous acid, H_2O, SO_2. On freezing this solution, a crystallized hydrate is obtained, which is thought to have the formula $H_2SO_3, 14H_2O$.

173. Chemical properties. Sulphurous anhydride rapidly extinguishes the flame of ordinary combustibles. If a pan of burning sulphur is placed at the base of a chimney on fire, the flame of the burning soot is extinguished. Nevertheless, many metals in a finely divided state burn when heated in an atmosphere of this gas.

A solution of sulphurous acid exposed to the air slowly takes up oxygen and becomes sulphuric acid. This tendency to absorb oxygen renders the acid and its salts powerful reducing agents. (See Exp. 31).

Exp. 118.—Add a few drops of sulphurous acid to a weak solution of potassium permanganate. The red color disappears.

174. Sulphurous acid is an excellent bleaching agent for wool, silk, and straw. The bleaching is not always permanent, since the acid does not seem to decompose the coloring matters, but to form unstable, colorless compounds with them; as, in course of time, the color reappears.

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* See Norton's Philosophy, Art. 577.

Exp. 119.—Add a little sulphurous acid to a decoction of red cabbage previously rendered green by a drop of potassium hydrate: the color disappears. Now divide the liquid into two portions: to the first, add potassium hydrate—the green reappears; to the second, add sulphuric acid—the liquid becomes red.

Exp. 120.—Place in a bell glass a bunch of damp flowers over a crucible containing burning sulphur. (Fig. 57). Many of the flowers will be bleached. On dipping some of them afterward into sulphuric acid, and others into ammonia, their colors will be partly restored, but generally modified, by the action of the acid or of the alkali.

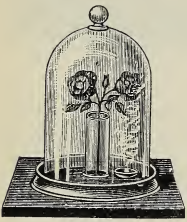

Fig. 57.

175. Sulphurous acid and its salts are valuable antiseptics; that is, they have the power of preventing or of arresting fermentation. For this reason cider barrels are "sulphured," in order to prevent the action of any substance capable of exciting fermentation in the new cider. For a similar reason calcium sulphite is frequently added to sweet cider. The air of rooms may be disinfected by burning sulphur in them.

Tests.—Free sulphurous acid is readily recognized by its odor. The sulphites evolve SO_2 when treated with dilute sulphuric acid. If zinc be added to this mixture, the SO_2 is reduced to H_2S, which may be recognized by blackening lead paper.

176. Uses. Sulphurous acid is used for its bleaching and antiseptic properties. The acid sodium sulphite, NaH,SO_3, is used by paper makers as an *antichlore*, to prevent a destruction of the fiber through an excessive action of chlorine in bleaching.

177. Sulphuric anhydride, SO_3, may be formed by passing a mixture of dried sulphurous anhydride and oxygen through a tube containing heated platinum sponge. It is prepared more conveniently from the Nordhausen oil of vitriol. On gently heating this, the

anhydride is disengaged, and may be collected in dry receivers cooled by ice.

178. Physical properties. Sulphuric anhydride crystallizes in white, feathery groups resembling asbestos. When perfectly dry it may be handled without inconvenience, and does not exhibit acid properties. Exposed to the air it absorbs water and becomes sulphuric acid. It is then very corrosive. Dropped into water it hisses like red-hot iron.

179. Chemical properties. The vapor of sulphuric anhydride passed over heated baryta or lime converts these bases into sulphates, with vivid incandescence.

180. Sulphuric acid, $H_2O, SO_3 = H_2SO_4$, has been found free in certain mineral waters, notably so in the Rio Vinagre of South America. It results, also, from the oxidation of sulphur and hydrogen sulphide.

181. Preparation. Sulphuric acid is prepared in enormous quantities by the oxidation of sulphurous anhydride in the presence of water.

Exp. 121.—Plunge into a jar of sulphurous anhydride a glass rod which has been dipped in fuming nitric acid. Red fumes appear, which show that the nitric acid has been reduced. In a little while the red color disappears, and a crystalline substance forms on the sides of the jar. Now, if a little water be shaken on the sides of the jar, the crystals dissolve with effervescence, the red fumes again appear, and the water contains sulphuric acid.

Exp. 122.—This process may be repeated on a larger scale by the apparatus shown in Fig. 58. A is a large globe fitted with a cork through which are passed five tubes, three of which are connected with the generating flasks, a, b, c.

I. The flask, b, contains copper filings. On pouring a very little nitric acid on these, nitric oxide is formed:

$$3\,Cu + 4\,(H_2O, N_2O_5) = 3\,(CuO, N_2O_5) + \widehat{N_2O_2} + 4\,H_2O.$$

II. When this nitric oxide is mixed with the air of the flask and of the globe, it forms red fumes which are nitrogen peroxide:

$$N_2O_2 + \text{air or oxygen} = N_2O_4.$$

III. When the globe is filled with the nitrogen peroxide, evolve sulphurous anhydride from the flask, a, containing copper and strong sulphuric acid.

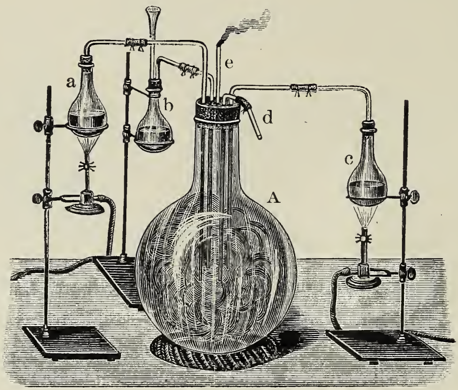

FIG. 58.

IV. The sulphurous anhydride will soon reduce the nitrogen peroxide to nitric oxide, the contents of the globe becoming colorless: $2\,SO_2 + N_2O_4 = 2\,SO_3 + N_2O_2$. The crystalline compound forms on the side of the flask. The structure of these crystals is unknown, but we may assume them to be $N_2O_2, 2\,SO_3$.

V. Now let steam be passed into the globe from the flask, c, which contains water. The crystals effervesce, and dilute sulphuric acid collects at the bottom of the globe.

$$N_2O_2, 2\,SO_3 + 2\,H_2O = 2\,(H_2O, SO_3) + N_2O_2.$$

The process is now finished. To render the process continuous, air must be blown from time to time through the tube, d, into the globe. The N_2O_2 liberated by the last reaction again becomes N_2O_4. Hence, but very little nitric oxide is necessary for the production of a large amount of sulphuric acid. It acts as a carrier of oxygen from the air to the sulphurous anhydride. The tube, e, allows the nitrogen of the air to escape.

It is scarcely necessary to mention, if these different steps occur simultaneously, that none of the crystalline compound will be deposited, as it is at once decomposed in the presence of water.

In sulphuric acid manufactories, the glass globe is replaced by a series of enormous leaden chambers. The sulphurous acid is generated by burning sulphur or iron pyrites in a furnace so arranged that the proper quantity of air may enter the chambers with the sulphurous anhydride. The nitric acid vapor is evolved from a mixture of sodium nitrate and sulphuric acid contained in an iron pan, which is heated by the combustion of the sulphur. Jets of steam are introduced at various parts of the chambers, and water is allowed to cover the floors. The sulphurous anhydride reduces the nitric acid, and combines with oxygen and water to form sulphuric acid. Provision is made to allow the nitrogen of the air, which takes no part in these changes, to escape, and, at the same time, to prevent loss by absorbing the nitrogen oxides for future use.

The acid is allowed to collect in the chambers until it has a specific gravity of 1.55. It is then drawn off and evaporated in leaden pans until it reaches the specific gravity of 1.72. Farther concentration is effected in platinum stills.

The commercial acid has a specific gravity of 1.82, and is known as oil of vitriol. This oil of vitriol frequently contains lead, arsenic, and other impurities.

182. Physical properties. Pure, concentrated sulphuric acid is an oily, colorless, inodorous liquid, having the specific gravity of 1.842. It boils at 327° C., and solidifies at —35° C. It is remarkable for its great attraction for water.

Exp. 123.—Place four ounces of water in a beaker, and pour into it a pint of strong sulphuric acid in a thin stream. The temperature often rises to 100° C. If the mixture be stirred with a thin test tube containing alcohol, the alcohol will boil.

When exposed to the air, sulphuric acid will often double its weight in a few days; hence it is often used as a desiccating agent.

Gases are dried by allowing them to pass over pumice stone

soaked in strong sulphuric acid, or through a bottle containing the acid. Other bodies are dried by placing them in shallow vessels over a dish of sulphuric acid, and covering the whole by a bell glass so as to exclude the air. By conducting this operation *in vacuo*, water may be frozen by its own evaporation.

183. Chemical properties. Sulphuric acid also abstracts water from many organic substances, charring them or giving rise to new compounds.

Exp. 124.—Drop a lump of sugar into strong sulphuric acid: in a short time it will become carbonized.

Organic tissues moistened with the dilute acid are destroyed, from the gradual concentration of the acid by evaporation.

Strong sulphuric acid is reduced to sulphurous acid when heated with charcoal, sulphur, or the ordinary metals. The metals are thereby converted to oxides which form sulphates with another portion of the acid (Exp. 116). On the other hand, metals of the zinc and iron groups, except copper, when treated with the dilute acid, displace the hydrogen to form their sulphates (§ **81**). The sulphates are also formed when the acid is made to act upon metallic oxides, or upon their compounds with nearly all other acids. The acid is, therefore, one of the most energetic known.

TESTS.—Free sulphuric acid and solutions of its salts give, with barium chloride, a white, insoluble precipitate. Similar precipitates are given by strontium chloride and calcium chloride.

184. Uses. Sulphuric acid is used in the preparation of most other acids, in the manufacture of soda, phosphorus, and alum, and is employed, directly or indirectly, in nearly all important chemical processes. It is the most important chemical reagent we have. Over 100,000 tons are annually consumed in Great Britain alone.

185. Nordhausen oil of vitriol is obtained by heating dried ferric sulphate in earthen retorts. The acid which distills over is probably a compound of sulphuric anhydride and sulphuric acid: $SO_3H_2SO_4 = H_2S_2O_7$.

186. Properties. Nordhausen acid fumes in the air when the bottle containing it is opened. It is a little heavier than the ordinary acid, and is usually of a brownish color. Its salts are sometimes called *anhydrosulphates*, as $K_2S_2O_7$.

187. Uses. It is used in making artificial alizarine, and for dissolving indigo in preparing Saxony blue.

188. Thiosulphuric acid, $H_2S_2O_3$, has not been isolated. Its salts are generally known as hyposulphites.

Sodium hyposulphite is prepared by boiling sodium sulphite with sulphur.

$$Na_2O, SO_2 + S = Na_2O, S_2O_2 \text{ or } Na_2S_2O_3.$$

It may be obtained in prismatic crystals, having the formula $Na_2S_2O_3, 5H_2O$.

Sodium hyposulphite is used for preparing other hyposulphites, and finds extensive employment in "fixing" photographic prints.

Exp. 125.—Prepare a little silver chloride by adding hydrochloric acid to silver nitrate, and wash with water by decantation. To one portion, suspended in water, add sodium hyposulphite. The silver chloride will change to silver hyposulphite, and dissolve: $2\,AgCl + Na_2S_2O_3 = 2\,NaCl + Ag_2S_2O_3$. Expose another portion to the sunlight; it darkens from the formation of a silver subchloride. On treating this with sodium hyposulphite, the silver subchloride is decomposed into silver chloride, which dissolves as before, and into metallic silver, which is left in a very finely divided state as a black powder. The photographer repeats this last process, except that he performs the operation upon paper which has been impregnated with silver chloride, and completes the process by washing out all the hyposulphite, so as to leave only the silver which has been reduced. (See § 398).

TEST.—The hyposulphites treated with hydrochloric acid evolve sulphurous anhydride, and deposit yellow sulphur.

189. Haloid compounds of sulphur. Sulphur forms compounds with chlorine, bromine, and iodine. One of these compounds—the disulphide of chlorine, Cl_2S_2—is employed as an agent in vulcanizing caoutchouc. It is a liquid formed by passing chlorine through the vapor of sulphur.

Comparison of Oxygen and Sulphur.

I. Oxygen and sulphur combine directly with most of the elements to form anhydrides.

Basic oxides; as, K_2O.	Basic sulphides; as, K_2S.
Indifferent oxides; as, MnO_2.	Indifferent sulphides; as, FeS_2.
Acid oxides; as, As_2O_3.	Acid sulphides; as, As_2S_3.

II. The anhydrides may unite together, forming—

Oxy-salts; as, K_2O, As_2O_3.	Sulpho-salts; as, K_2S, As_2S_3.

III. They may also combine with H_2O or with H_2S to form—

Hydrates; as, K_2O, H_2O.	Sulpho-hydrates; as, K_2S, H_2S.

Heat alone decomposes:

The oxides and sulphides of the noble metals; as, PtO_2, PtS_2.
Many of the higher oxides and sulphides; as, I_2O_5, I_2S_2.
And reduces some; as, MnO_2 to Mn_3O_4, and FeS_2 Fe_3S_4.

Hydrogen nascent, or passed over heated oxides and sulphides, reduces many of them.

$CuO + H_2 = Cu + H_2O$. $\qquad Ag_2S + H_2 = 2Ag + H_2S$.

Heated carbon reduces the oxides and sulphides of most metals.

$Fe_2O_3 + 3\,C = Fe_2 + 3\,CO$. $\qquad 2\,FeS + C = 2\,Fe + CS_2$.

Chlorine may also decompose them, uniting with the more electro-positive element.

$H_2O + Cl_2 = 2\,HCl + O$. $\qquad H_2S + Cl_2 = 2\,HCl + S$.

CHAPTER VII.

THE NITROGEN GROUP.

ELEMENT.	SYMBOL.	SPECIFIC GRAVITY. SOLID. $H_2O=1$.	AËRIFORM. AIR = 1.	AËRIFORM. H = 1.	ATOMIC WEIGHT.	FUSING POINT. °C.	DISCOVERER.
Nitrogen	N		0.969	14	14.		Rutherford, 1772.
Phosphorus	P	1.83	4.29	62	31.	44°	Brandt, 1669.
Vanadium	V	5.5			51.3		Sefström, 1830.
Arsenic	As	5.73	10.34	150	75.	180°	Schröder, 1694.
Antimony	Sb	6.7		244?	122	450°	Valentine, ?1480.
Bismuth	Bi	9.9			210	264°	Agricola, 1529.
Niobium	Nb	6.27			94.		Hatchett, 1801.
Tantalum	Ta	10.78			182		Ekeberg, 1802.

190. The members of this group yield analogous compounds, as exhibited in the following schedule:

HYDRIDES, . .	H_3N,	H_3P,	H_3As,	H_3Sb.	
CHLORIDES, . .	NCl_3,	PCl_3,	$AsCl_3$,	$SbCl_3$,	$BiCl_3$.
ANHYDRIDES,	N_2O_3,	P_2O_3,	As_2O_3,	Sb_2O_3,	Bi_2O_3.
	N_2O_5,	P_2O_5,	As_2O_5,	Sb_2O_5,	Bi_2O_5.

191. The hydrides are fetid, inflammable gases, in which three atoms of hydrogen are united with one atom of the other element, and condensed to two volumes. No hydrides of vanadium or bismuth are known, but there exists a complete series of trichlorides. These compounds indicate that the elements of this group are triads; but they also play the part of pentads in a number of compounds, and hence are variously classed by chemists as triad and as pentad elements. All of

these elements form at least two compounds with oxygen.

192. Vanadium is quite rare. It has chlorides which are both perissads and artiads, as VCl_2, VCl_3, and VCl_4,—which is an unexplained anomaly. Niobium, sometimes called columbium, and tantalum are still rarer elements.

NOTE.—All these agree in forming oxides of the formula R_2O_5, and other compounds which place them in this group. They are, however, not of sufficient importance to be considered further.

193. The other elements of the group manifest the gradational character noticed in the preceding groups. Nitrogen and phosphorus are, without doubt, non-metals: bismuth presents all the physical characters of the metals: arsenic and antimony may be considered as semi-metals, or as a connecting link between the non-metals and the metals. They have many of the physical properties of the metals and the chemical properties of the non-metals. Arsenic very closely resembles phosphorus in its oxygen compounds, and antimony in its sulphides and in its physical properties. Its atomic weight is also very nearly the mean between the two others. Similarly, antimony is allied on the one hand to phosphorus, and on the other to bismuth.

The sesquioxides of this group are acid anhydrides in nitrogen, phosphorus, and arsenic, feebly acid or feebly basic in antimony, and basic in bismuth. The highest oxides are all acid anhydrides, but the acid properties of bismuthic oxide are very feeble.

NITROGEN.

194. Nitrogen forms four-fifths of the volume of the air. The air also contains traces of ammonia, NH_3. It is found in most animal and in many vegetable sub-

stances. It also occurs in the form of sodium and potassium nitrates, and of the ammoniacal salts.

195. Preparation. Nitrogen may be obtained from the air by potassium pyrogallate (Exp. 78), or by burning in it any substance which forms with oxygen a product that may easily be removed.

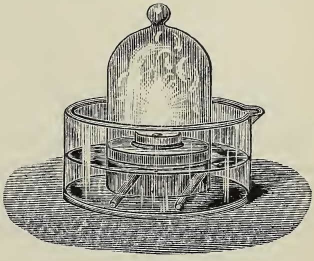

FIG. 59.

Exp. 126.—Place a dried slice of phosphorus in a capsule; float it on the surface of water, and ignite it. Now cover it with a bell glass. The oxygen within the bell will be consumed, and white clouds of phosphoric anhydride be formed. These will soon be absorbed by the water, and the gas remaining is nearly pure nitrogen. Nitrogen may also be obtained by boiling a solution of potassium nitrite mixed with thrice its volume of a strong solution of ammonium chloride: $NH_4Cl + KNO_2 = KCl + 2H_2O + 2\overset{\frown}{N}$. (See § 722.)

196. Physical properties. Nitrogen is a colorless, odorless, tasteless, permanent gas.

197. Chemical properties. Free nitrogen is remarkable for its chemical inactivity. It is neither combustible nor a supporter of combustion. At elevated temperatures it combines with titanium, carbon, oxygen, and a few other elements. It also unites with nascent hydrogen: thus, when iron rusts in moist air, a little ammonia is frequently found absorbed by the ferric oxide.

The organic compounds of nitrogen are exceedingly prone to decomposition. The mineral compounds are often unstable and explosive, as is especially the case with those that contain the radical nitryl (NO_2). This character of instability renders many of the nitrogen compounds energetic chemical agents.

TESTS.—A gas which does not give any reaction with any known chemical test may be pronounced nitrogen. Solid organic matters containing nitrogen, when heated with a mixture of caustic soda and lime, yield ammonia H_3N.

198. Uses. The use of free nitrogen in the air appears to be to prevent the too rapid action that would take place in pure oxygen.

AMMONIA, H_3N.

199. Ammoniacal compounds are but sparingly found in nature, although ammonia is constantly produced in the putrefaction of animal and vegetable matters. The reason for this seems to be that plants derive their chief supply of nitrogen from the salts of ammonia, which are brought down by the rain from the atmosphere, and so consume it as rapidly as it is formed.

200. Preparation. The commercial source of ammonia and its compounds is the so-called sal-ammoniac , or ammonium chloride, NH_4Cl. This is obtained in large quantities in the process of making illuminating gas from coal.

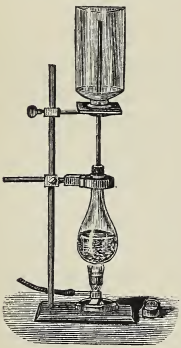

FIG. 60.

Exp. 127.—Rub together 30 grammes of pulverized sal ammoniac and 60 grammes of powdered quicklime. The heat caused by the friction will be sufficient to evolve the gas.

Exp. 128.—To collect the gas, pour this mixture into a flask to which a tube has been fitted; then add 60 cc. of water, and heat. Collect by upward displacement. (Fig. 60). It may be dried by passing it through a bottle containing lumps of quicklime.

$$2(NH_4Cl) + CaO = CaCl_2 + H_2O + 2H_3N.$$

Exp. 129.—It may also be collected for purposes of experiment by gently heating aqua ammonia and drying the gas.

201. Physical properties. Ammonia is a colorless, coercible gas of a pungent odor: sp. gr. 0.59. Aqua ammonia is a solution of the gas in water, obtained by passing a stream of the gas through bottles containing water, and kept cool by ice. One volume of water at 15° C. absorbs 783 volumes of the gas, and increases in volume one-half: sp. gr. 0.85. This solution is the aqua ammonia of commerce. The amount of the gas retained in the solution varies with the temperature and pressure.

Exp. 130.—Fill a barometer tube over 30 inches long with one inch of concentrated aqua ammonia and sufficient mercury to occupy the remaining space, and invert the tube under mercury. On removing the finger the Torricellian vacuum will be formed, and the ammonia solution will boil from the escape of a large quantity of the gas. (Fig. 61). The gas may be re-absorbed on depressing the tube in a tall cylinder of mercury, because of the increased pressure. It may then be re-expelled by pouring hot water on the top of the tube.

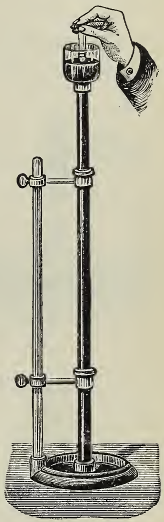

Fig. 61.

Exp. 131.—To show the rapid absorption of ammonia by water, Exp. 95 may be repeated with dry ammonia gas.

The gas may be condensed at —40° C. to a clear liquid which solidifies at —75° C. It may also be liquefied at 10° C. by a pressure of six atmospheres. The liquid evaporates rapidly and absorbs a large amount of heat. Carré's freezing apparatus utilizes these properties of ammonia in the production of artificial ice.

202. Chemical properties. The feeble combustible power of ammonia has already been shown in Exp. 49. Both the gas and the solution have strong alkaline properties, which will be considered in the chapter on alkalies.

TESTS.—Free ammonia is detected (1) by its odor; (2) by its action on moistened red litmus paper; (3) by giving white fumes of NH_4Cl when a glass rod dipped in HCl is brought in contact with it.

Ammoniacal salts yield free NH_3 when heated with soda-lime or with KHO. *Traces* of aqua ammonia or of ammoniacal salts are detected by forming a brownish precipitate on the addition of "Nessler's test."*

203. Ammonia derivatives. Each of the hydrogen atoms in ammonia may be exchanged for a monad radical (elementary or compound), and thus give rise to new compounds which may be considered as formed on the type of one or more molecules of ammonia.

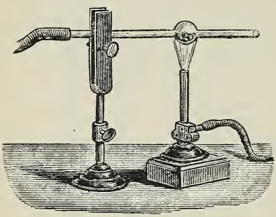

FIG. 62.

(I) When a positive radical takes the place of the hydrogen, an *amine* compound is formed. Thus, potassamine forms when dry ammonia gas is passed over a clean pellet of potassium, gently heated.

$$H_3N + K = KH_2N + H.$$

If potassamine is strongly heated, it becomes tripotassamine: $3KH_2N = K_3N + 2H_3N$.

(II) When a negative radical takes the place of the hydrogen, an *amide* compound is formed.

Exp. 132.—Rub together a gramme of iodine and 16 cc. of aqua ammonia. On standing for thirty minutes, a brown powder, usually called iodide of nitrogen, is formed.

$$3H_3N + I_4 = \underline{I_2HN} + 2(NH_4I).$$

*This is prepared by adding to a gramme of KI, dissolved in H_2O, enough $HgCl_2$ to re-dissolve the precipitate which forms. Four grammes of KHO are then added, and water enough to make the volume of 100 cc. The liquid is then allowed to stand until it becomes clear, and the solution is preserved in tightly corked bottles.

$$4HgK_2I_4 + 6KHO + 2(NH_3H_2O) = \underline{Hg_4N_2I_2, 2H_2O} + 14KI + 6H_2O.$$

It may also be termed di-iodamide. Collect the powder on a filter, divide it into four or five portions, and suffer them to dry in a quiet place. When dry, it explodes if touched even by a feather.

A chloride of nitrogen, Cl_3N, Cl_2HN, or a trichloramide may be formed by exposing sal-ammoniac to the action of chlorine gas. It is so violently explosive that none but expert chemists should attempt to prepare it.

(III) These derivative compounds are sometimes called *amides*, *imides*, and *nitriles*, as if formed from the radicals, NH_2 (amidogen), NH (imidogen), and trivalent nitrogen.

204. There are also derivatives containing both positive and negative radicals, which are called *alkalamides*. In some ammoniacal compounds the nitrogen appears to be pentavalent, as sal-ammoniac, NH_4Cl. If ammonia be added in excess to mercuric chloride, a white precipitate forms of the formula $N^{v}{}_2H'_4Hg''_2Cl'_2$ (dimercuric dichloramide). If ammonia be added to freshly precipitated mercurous chloride, black mercurous chloramide ($N^{v}H'_2Hg'_2Cl'$) forms. Both of these are alkalamide compounds.

Compounds of Nitrogen and Oxygen.

205. There are five oxides of nitrogen, viz:

Protoxide, or nitrous oxide, N_2O.
Dioxide, or nitric oxide, N_2O_2; nitrosyl $(NO)'$.
Teroxide, or nitrous anhydride, N_2O_3.
Tetroxide, or nitric peroxide, N_2O_4; nitryl $(NO_2)'$.
Pentoxide, or nitric anhydride, N_2O_5.

Three of these oxides unite with water to form acids:

$N_2O + H_2O = H_2O, N_2O$ or $2\,(HNO)$, hyponitrous acid.
$N_2O_3 + H_2O = H_2O, N_2O_3$ or $2\,(HNO_2)$, nitrous acid.
$N_2O_5 + H_2O = H_2O, N_2O_5$ or $2\,(HNO_3)$, nitric acid.

The dioxide and the trioxide have no corresponding acids. All of these oxides are obtained from nitric acid.

206. The nitrates are formed by the oxidation of nitrogenous organic matters in the presence of strong bases. Potassium nitrate, or saltpeter, occurs native in India, and is also largely manufactured by the decomposition of other crude nitrates. Sodium nitrate, or Chili saltpeter, occurs in large beds in South America. Rain-water also contains traces of nitrates, which may come either from the oxidation of ammonia or from the action of atmospheric electricity.

207. Nitric acid is a monobasic acid, having the formula HNO_3; but we shall frequently find it convenient to use the binary formula H_2O, N_2O_5, which contains two molecules. It is obtained by distilling a nitrate with strong sulphuric acid.

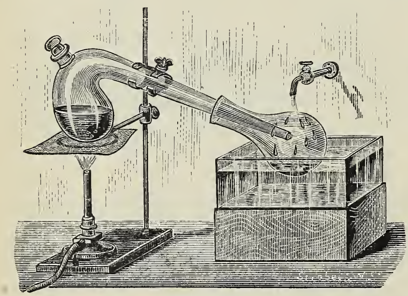

Fig. 63.

Exp. 133. — Heat equal weights of saltpeter and strong sulphuric acid, and collect the distillate in a receiver kept cool by water. Red fumes appear at the beginning of the process, but afterward a nearly colorless acid collects in the receiver. (Fig. 63).

$$KNO_3 + H_2SO_4 = KHSO_4 + H\overset{\frown}{N}O_3.$$

When the distillation has ceased, and the retort has somewhat cooled, warm water may be added and the solution poured out. This yields, on evaporation, crystals of acid potassium sulphate. When half the quantity of sulphuric acid is used, the same reaction takes place in the first stages, but afterward the acid sulphate acts upon the saltpeter remaining to form normal potassium sulphate: $KHSO_4 + KNO_3 = K_2SO_4 + H\overset{\frown}{N}O_3$. This, however, is not advantageous, because the heat required is so great as to decompose a part of the nitric acid, and because the normal sulphate is less easily removed from the retort.

208. Physical properties. Pure nitric acid is a colorless, volatile liquid of the specific gravity 1.52. It solidifies at $-55°$ C., and boils at 86° C. Nitric acid is usually more or less colored, owing to the absorption of the lower oxides of nitrogen, which are the products of its own partial decomposition. Red fuming nitric acid is the strong acid containing a considerable quantity of pernitric oxide. The ordinary *aqua fortis* contains from 30 to 60 per cent of nitric acid.

209. Chemical properties. Nitric acid is easily decomposed into water, oxygen, and a lower oxide of nitrogen. For this reason it is a powerful oxidizing agent.

Exp. 134.—Pour a little of the strongest nitric acid upon warm, powdered charcoal: the latter takes fire at once.

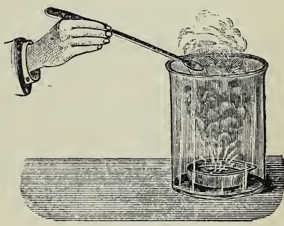

FIG. 64.

Exp. 135.—Drop a small pellet of phosphorus into the strongest nitric acid (placed at some distance from the operator, to avoid danger). It oxidizes, and frequently with such violence as to burst into flame. (Fig. 64).

In like manner, sulphur and iodine, when heated with nitric acid, are converted to sulphuric and iodic acids. When nitric acid is poured upon the ordinary metals, it oxidizes them and is itself reduced to one of the lower oxides of nitrogen. The usual reactions may be illustrated by the following experiments.

Exp. 136.—Add nitric acid to tin foil. The latter is converted into white metastannic acid.

$$10(H_2O, N_2O_5) + 5Sn = Sn_5O_{10}, 10H_2O + 10N_2O_4.$$

The red fumes are nitric peroxide. If the white tin powder be mixed with slaked lime and gently warmed, ammonia will be given off, showing that a portion of the acid has been converted into H_3N.

Exp. 137.—Add strong nitric acid to copper clippings. A portion of the acid will be reduced to nitric oxide, and cupric oxide is formed: another portion unites with the cupric oxide to form blue cupric nitrate.

$$4(H_2O, N_2O_5) + 3Cu = 3(CuO, N_2O_5) + 4H_2O + N_2O_2.$$

This is the usual reaction with the metals. The nitric oxide is itself colorless, but is converted by contact with the air into red nitric peroxide. (See § **392**).

Nitric acid acts energetically upon organic matters. (1) It oxidizes them: thus, indigo is converted to isatin, and is thereby bleached. Starch and sugar are converted to oxalic acid. (2) It forms substitution products through the displacement of one or more atoms of hydrogen in the original compound by the radical nitryl $(NO_2)'$. Thus, benzole, C_6H_6, treated with strong nitric acid, becomes nitro-benzole, $C_6H_5(NO_2)$; phenol, or carbolic acid, C_6H_6O, yields tri-nitro-phenol, or picric acid, $C_6H_3(NO_2)_3O$. This latter substance is a permanent yellow dye. Nitric acid stains the skin and many other organic substances yellow, probably from the formation of picric acid.

Exp. 138.—Dip a skein of white silk thread into dilute nitric acid for a few minutes; then wash thoroughly with water. It will be colored permanently yellow.

The Tests for free nitric acid are: (1) its bleaching power upon indigo; (2) the red fumes which it evolves when added to copper filings. The normal nitrates are all soluble in water. Nitric acid in combination is detected by warming the nitrates with strong sulphuric acid, and applying either of the above tests. (3) By adding to the mixture, when cold, a crystal of ferrous sulphate. A brownish color indicates the presence of nitric oxide. (Exp. 142).

210. Nitric anhydride, N_2O_5, may be obtained by very gently heating silver nitrate in a slow current of dry chlorine gas. It is a crystalline, unstable solid, which readily unites with water to form nitric acid.

211. The uses of nitric acid as an energetic oxidizing agent have already been indicated. Its substitution products, gun cotton and nitro-glycerine, are very powerful explosive compounds. Nitro-benzole is used as an artificial perfume, and as a material from which aniline can be made. Engravers employ the acid for etching designs upon copper and steel. It attacks all the metals except gold and the metals of the platinum group.

212. Aqua regia is a mixture of one part of nitric acid with three parts of hydrochloric acid. The two liquids react upon each other and liberate chloronitric gas and free chlorine.

$$H_2O, N_2O_5 + 6HCl = 2NOCl_2 + 4H_2O + Cl_2.$$

A small quantity of chloronitrous gas, $NOCl$, is formed at the same time. The presence of the free chlorine renders aqua regia a solvent for gold and platinum. It should be prepared as wanted for use.

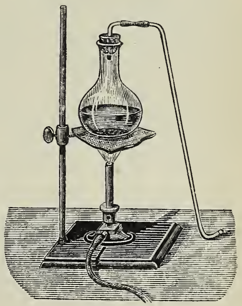

Fig. 65.

213. Nitrous oxide, N_2O, is prepared by gently heating ammonium nitrate. The salt readily melts and soon appears to boil, and is entirely decomposed into water and nitrous oxide.

$$NH_4, NO_3 \text{ heated} = 2H_2O + N_2O.$$

214. Physical properties. Nitrous oxide is a colorless, coercible gas, having a faint odor and a sweetish taste: sp. gr. 1.53. It liquefies at 7° C., under a pressure of 40 atmospheres, and solidifies at —100° C. The lowest temperature yet attained, —140° C., was produced by evaporating *in vacuo* a mixture of liquid nitrous oxide and carbon disulphide. The gas may be collected by displacement or over warm water. Water at 15° C. absorbs three-fourths of its volume of the gas.

215. The chemical properties of nitrous oxide resemble those of oxygen; but it does not form red fumes with nitric oxide.

Exp. 139.—Into jars of the gas, plunge (1) an ignited splinter of wood—it will burst into flame: (2) sulphur or phosphorus heated in a deflagrating spoon—the combustion will be very brilliant.

216. The physiological properties of the gas have given it the name of "laughing gas," because, when breathed in moderate quantity, it produces stimulating effects. Breathed in large quantity, it produces temporary stupor, and is used as an anæsthetic in dental surgery.*

The hyponitrite of sodium (NaNO) is formed by adding sodium amalgam to a solution of sodium nitrate. If the excess of the alkali be neutralized by acetic acid, the hyponitrous acid is liberated, but immediately decomposes to water and nitrous oxide:

$$2\,HNO = H_2O + N_2O.$$

217. Nitric oxide, N_2O_2 or NO, is usually prepared by treating copper clippings or mercury with moderately dilute nitric acid. (Exp. 137.) The gas may be collected over water, which absorbs the red fumes formed by the union of the NO with the air in the generating flask.

218. Physical properties. Nitric oxide is a colorless, gas (sp. gr. 1.04), very slightly soluble in water, which liquefies under a pressure of 146 atmospheres.

219. Chemical properties. Nitric oxide may be considered as the free state of the monatomic radical nitrosyl (NO). It is one of the most stable of the nitrogen oxides. Ordinary combustibles do not burn in it; but phosphorous or carbon, when burning briskly, is able to decompose the gas and combine with its oxygen.

Exp. 140.—Into a jar of the gas plunge a piece of dried phosphorus just ignited: it will be extinguished. Again introduce the phosphorus when in full combustion: it will burn as in oxygen.

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*Caution.—If the gas is to be used for inhalation, the ammonium nitrate should be free from sal-ammoniac, as, otherwise, it will be mixed with chlorine.

The special characteristic of nitric oxide is its strong attraction for free oxygen. It unites directly with it, producing deep red fumes which are chiefly nitric peroxide, N_2O_4, but mixed with nitrous anhydride, N_2O_3.

Exp. 141.—Fill a small jar with blue litmus water, and decant into it a pint of oxygen. Now add a pint of nitric oxide. Red fumes are formed which are soon absorbed by the water. Now add another pint of nitric oxide. If both the oxygen and the nitric oxide are pure, the gases will be completely absorbed by the water, showing that nitric peroxide is formed by the union of two volumes of nitric oxide with one of oxygen. The litmus becomes red.

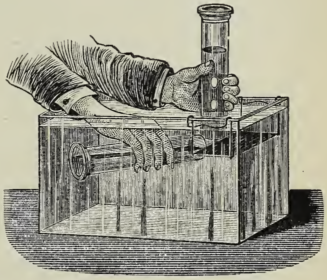

FIG. 66.

Owing to this ready combination with oxygen, the actual taste, odor, and respirability of nitric oxide have not been ascertained.

Nitric oxide is readily absorbed by solutions of the ferrous salts, forming compounds such as $2FeSO_4, NO$.

Exp. 142.—Shake a little ferrous sulphate in a jar of the gas: a brown solution will be formed, which, on exposure to the air or on warming, soon becomes colorless.

220. Nitrous anhydride, N_2O_3, is best prepared by gently heating nitric acid with an equal weight of arsenious acid, and collecting the distillate in a U tube surrounded by a freezing mixture.

$$H_2O, N_2O_5 + As_2O_3 = H_2O, As_2O_5 + N_2O_3.$$

221. Physical properties. The nitrous anhydride thus obtained is a blue liquid, easily decomposed by heat, and forming with water at 0° C. a blue liquid which is nitrous acid, H_2O, N_2O_3 or HNO_2.

222. Nitrous acid is stable only at low temperatures or in very dilute solutions. When heated, it decomposes into nitric oxide, which escapes with effervescence, and into nitric acid and water, which remain in the solution.

The alkaline nitrites are produced by heating the alkaline nitrates to redness. Oxygen is given off; a mixture of free alkali and nitrite remains.

Exp. 143.—Heat potassium nitrate in a crucible until a portion, removed on the end of an iron rod, gives a strong alkaline reaction. Then pour the fused mass on a dry stone, and, when cooled, preserve the potassium nitrite in stoppered bottles.

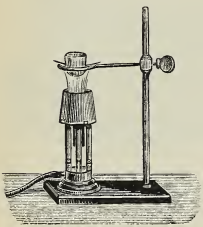

Fig. 67.

Nitrous anhydride is disengaged when a nitrite is treated with a dilute acid. It is, however, almost immediately decomposed into nitric oxide and nitric acid. The acidulated solutions of the nitrites act:

(I) As reducing agents.

Exp. 144.—To a solution of potassium permanganate, add a few drops of sulphuric acid and then a solution of potassium nitrite. The red color disappears: MnO, SO_3 is formed.

(II) As oxidizing agents.

Exp. 145.—To a dilute indigo solution, add a solution of potassium nitrite and then a few drops of sulphuric acid. The indigo is changed to isatin and bleached.

Exp. 146.—To a solution of potassium iodide, add the nitrite and acidulate. The potassium is oxidized and the iodine set free. The iodine may be detected by starch paste, or dissolved out of the aqueous solution by carbonic disulphide.

Tests.—The above reactions are also tests for nitrous acid. The nitrites are distinguished from the nitrates by giving, with ferrous salts, a brown discoloration without the addition of an acid.

223. When ammonia is burned in the air it is decomposed, and both of its constituents unite with oxygen — the hydrogen to form water, the nitrogen to form nitrous anhydride or some other oxide of nitrogen.

Exp. 147.—Shake copper filings, with a little strong aqua ammonia, in a large flask. White fumes will be produced, the liquid will become blue, and will be found to contain oxide of copper and nitrite of ammonia.

Exp. 148.—Suspend a highly heated coil of thin platinum wire in a flask containing a little strong aqua ammonia. Thick, white clouds of ammonium nitrite are formed, and sometimes red vapors of nitrous anhydride. If a tube delivering oxygen be passed into the flask, the action will be more energetic. The spiral will glow for some time, the red fumes will be more abundant, and little explosions rapidly succeed one another.

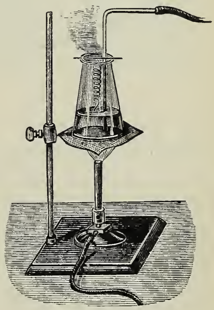

FIG. 68.

224. Nitric peroxide, N_2O_4 or NO_2, has already been mentioned as forming the greater part of the red fumes which are produced by the action of oxygen upon nitric oxide.

225. Physical properties. It is possible to condense these fumes into a crystalline solid which melts at —9° C., or to a volatile, almost colorless liquid whose color changes, as the temperature rises, from a greenish yellow to yellow, and then to orange. At 22° C. it boils and forms red vapors, which may become so dark as to be almost opaque. These vapors are irrespirable, and have a pungent, suffocating odor.

226. Chemical properties. Although ordinary combustibles are extinguished by nitric peroxide, it is an energetic oxidizing agent. Its use in converting sulphurous to sulphuric acid has already been mentioned. In the

presence of water it is decomposed into nitrous and nitric acids, with the formation of a liquid whose color varies from green to blue, according to the proportion of nitrous acid and unaltered nitric peroxide present. The same coloration is frequently observed when silver, mercury, or lead is dissolved in nitric acid, sometimes leading the novice to suspect the presence of copper.

Nitric peroxide acts as the free molecule of the monatomic radical *nitryl*, NO_2, which is capable of replacing hydrogen in many organic compounds.

PHOSPHORUS.

227. Phosphorus is never found uncombined in nature, but is very widely and abundantly diffused in the form of phosphates. Calcium phosphate, the chief source of this element, is found in guano, coprolites, and in apatite. It is also found in small quantities in all arable soils, whence it is taken up by plants and accumulated in their seeds. The animals which feed upon these seeds assimilate it, and hence it forms a part of almost every solid and liquid in the bodies of animals. The bones of oxen contain nearly 58 per cent of calcium phosphate and 2 per cent of magnesium phosphate. When bones are burnt they leave a white and friable ash, which is impure tri-calcium phosphate, $3\,CaO, P_2O_5$.

228. Preparation. Phosphorus and its compounds are obtained from this "bone ash."

(1) The ground bones are digested for some hours with two-thirds their weight of strong sulphuric acid and six times their weight of water. An insoluble calcium sulphate and a soluble monocalcic phosphate, or "superphosphate of lime," are formed.

$$3\,CaO, P_2O_5 + 2\,(H_2O, SO_3) = 2\,(CaOSO_3) + CaO, 2\,H_2O, P_2O_5.$$

(2) The calcium sulphate is removed by filtration. The solution is then evaporated to a syrup, and is then mixed with one-fourth

of its weight of charcoal, and heated to redness. The monocalcic phosphate is converted into calcium meta-phosphate, CaO, P_2O_5.

$$CaO, 2\,H_2O, P_2O_5 \text{ heated} = CaO, P_2O_5 + 2\,\widehat{H_2O}.$$

(3) On distilling this mixture of charcoal and calcium metaphosphate in a retort, phosphorus is set free, passes over in vapor, and may be condensed under water. The calcium retains enough of the acid to reconvert it into tricalcic phosphate.

$$3\,(CaO, P_2O_5) + 10\,C = 3\,CaO, P_2O_5 + 10\,\widehat{CO} + \widehat{P_4}.$$

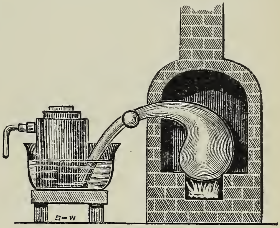

FIG. 69.

(4) The crude phosphorus thus prepared is purified by melting it under water containing a little chromic acid. It is then run into a horizontal tube surrounded by cold water, by which it is chilled, and is then drawn out in solid sticks.

229. Physical properties. Pure phosphorus, when first made, is an almost colorless, translucent solid: sp. gr. 1.82. It melts at 44° C., and boils in closed vessels at 290° C. The vapor density at 500°, referred to the hydrogen unit, is 62.1, which is double its atomic weight; from which it appears that the atom of phosphorus occupies only half the volume of the hydrogen atom, or that the molecule of phosphorus contains four atoms.

Phosphorus is somewhat soluble in turpentine and in essential and fixed oils. It is readily dissolved by carbonic disulphide. If this solution be evaporated in an atmosphere of carbonic anhydride, the phosphorus may be obtained in dodecahedral crystals.

230. Chemical properties. Phosphorus exposed to the air at ordinary temperatures undergoes a slow combustion, and is feebly luminous in the dark. Hence its name, which means the light-bearer (φῶς, φέρω). It is extremely inflammable, taking fire in the air a little above its melting point. (Compare Exp. 48). On this

account it is kept under water, and should be handled with great caution.

Phosphorus combines readily with many of the elements. (Exps. 10, 74, 88). Its compounds with the metals are called phosphides or phosphurets. Owing to the strong affinity of phosphorus for oxygen, it is an energetic reducing agent, and is capable of precipitating copper, lead, and some other metals from solutions of their salts.

Exp. 149.—Place a pellet of phosphorus in a solution of silver nitrate. In a few days it will be covered with metallic silver.

231. Phosphorus is capable of assuming several allotropic states, the most remarkable of which is the red, or amorphous, phosphorus. This may be prepared by heating ordinary phosphorus in an atmosphere of carbonic anhydride, at a temperature of 230° to 235° C., for thirty hours. The two modifications differ so much that we should suppose them to be different elements if we could not convert one into the other. The red phosphorus has a specific gravity of 2.14, is insoluble in carbon disulphide, does not inflame by friction, is unaltered in the air, and is not poisonous. If heated to 260° C., it is converted into ordinary phosphorus and bursts into a flame.

Ordinary phosphorus is very poisonous. Cases have occurred in which children have been poisoned by sucking the phosphorus combination on the tips of matches. Its vapor sometimes causes a necrosis of the jaw-bone. The best antidote is calcined magnesia.

232. Uses of phosphorus. "Lucifer matches" are made by tipping small wooden sticks with sulphur or paraffine, to convey the flame, and, afterward, with a composition containing ordinary phosphorus, glue, and an oxidizing substance like saltpeter or potassium chlorate. These matches take fire when rubbed on any rough surface.

"Safety matches" are tipped with a mixture of antimonous sulphide and potassium chlorate. These do not readily take fire by friction, but inflame when they are rubbed on a surface containing amorphous phosphorus, manganese dioxide, and fine sand.

Various attempts have been made to manufacture matches without phosphorus. Good matches have been made with a composition of potassium chlorate and lead hyposulphite.

A very common rat poison is made from ordinary phosphorus mixed with flour paste.

233. Tests. Free, ordinary phosphorus may be detected by its luminosity in the dark; phosphorus in combination, by heating the dry powder which contains it in a thin glass tube with a small bit of magnesium or sodium. On breaking the tube and adding water, the odor of hydrogen phosphide will be perceived, and frequently, also, its flame. Any one of its allotropic forms may be detected by oxidizing it to phosphoric acid, and applying the test for that body.

234. Compounds of phosphorus and hydrogen. Three of these compounds are known: (1) a solid phosphide, HP_2(?); (2) a spontaneously inflammable liquid phosphide, H_2P; and (3) gaseous phosphide, H_3P, generally called phosphuretted hydrogen.

235, Phosphuretted hydrogen is usually obtained by heating phosphorus in a strong alkaline solution.

Exp. 150.—Place in a small flask a few slices of phosphorus, and fill the flask with a strong solution of caustic potash. The evolution tube should dip under warm water. On gently heating the flask, bubbles of the gas mixed with free hydrogen escape into the air, and spontaneously inflame, with the production of beautiful white rings of phosphoric anhydride. (Fig. 70).

$$P_4 + 3H_2O + 3KHO = 3(KPH_2O_2) + H_3P.$$

236. Physical properties. Phosphuretted hydrogen is a colorless, coercible gas: sp. gr. 1.19. It has an offensive odor, being the same as that evolved by putrid fish.

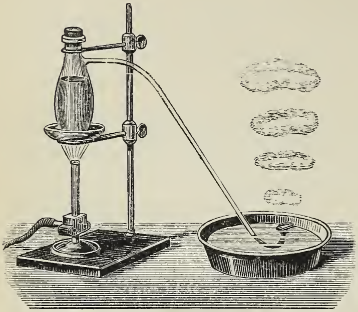

Fig. 70.

237. Chemical properties. The gas is not spontaneously inflammable. This property is given it by the presence of a small quantity of the liquid phosphide of hydrogen, and is lost when the gas is passed through a freezing mixture, or by admixture with the oil of turpentine. It is a very poisonous gas.

When the gas is passed into solutions of copper, a black precipitate of copper phosphide is formed. This phosphide, heated in a solution of potassium cyanide, evolves self-lighting phosphuretted hydrogen.

Tests.—Its odor is very characteristic. Salts of silver and gold are reduced to the metallic state by this gas.

238. The terchloride, PCl_3, forms when phosphorus is burned in chlorine; or, if the chlorine be in excess, the pentachloride, PCl_5. Both are decomposed by water, the latter forming an oxychloride, $POCl_3$. Phosphorus also combines with bromine, iodine, and sulphur. These compounds are of great importance in organic chemistry in forming "substitution compounds."

239. The oxygen compounds of phosphorus. Besides a suboxide of phosphorus, P_4O, which is imperfectly known, two anhydrides of phosphorus have been obtained as bulky, white, amorphous powders, by burning phosphorus in dry air. If the combustion is very slow,

the greater part of the product is phosphorous anhydride, P_2O_3: if the combustion is very rapid, the product is almost pure phosphoric anhydride, P_2O_5. Both of these anhydrides may be made to combine with three molecules of water to form:

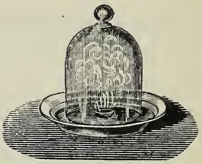

FIG. 71.

$3H_2O, P_2O_3$ or H_3PO_3 = phosphorous acid,

$3H_2O, P_2O_5$ or H_3PO_4 = phosphoric acid.

In the case of the phosphoric anhydride, it first becomes

Metaphosphoric acid, H_2O, P_2O_5 or H, PO_3,

which is converted, upon boiling with water, into

Pyrophosphoric acid, $2H_2O, P_2O_5$ or $H_4P_2O_7$,

and finally to the

Orthophosphoric acid, $3H_2O, P_2O_5$ or H_3PO_4.

Hypophosphorous acid, H, PH_2O_2, for which no corresponding anhydride is known, is another acid. The basicity of these acids varies from one to four, and is expressed by the hydrogen at the left of their formulæ.

240. The alkaline hypophosphites are formed by boiling phosphorus in alkaline solutions, as in Exp. 150. The aqueous solution of hypophosphorous acid is obtained by decomposing barium hypophosphite with sulphuric acid.

The acid and the alkaline hypophosphites are energetic reducing agents. They form, with silver nitrate, a white precipitate which quickly becomes black, metallic silver. When the dry salts are heated, they are converted into phosphates, and evolve phosphuretted hydrogen.

241. An impure phosphorous acid is obtained by exposing sticks of phosphorus to the action of moist air. The solution readily absorbs oxygen, and is changed to

phosphoric acid. It reduces silver nitrate like the hypophosphites, but less energetically.

242. Orthophosphoric acid is prepared by oxidizing phosphorus with nitric acid.

$$5(H_2O, N_2O_5) + 4H_2O + P_6 = 3(3H_2O, P_2O_5) + 10\overset{\frown}{N}O.$$

This solution evaporated at a gentle heat forms a syrupy liquid, from which, by evaporating *in vacuo*, hard, transparent crystals may be obtained, called orthophosphoric acid. The formula is $3H_2O, P_2O_5$ or H_3PO_4. This is the ordinary phosphoric acid, and is tribasic.

If the solution of orthophosphoric acid be heated to 215° C., one equivalent of water is expelled and *pyro-phosphoric acid* is formed, which has the formula, $2H_2O, P_2O_5$ or $H_4P_2O_7$, and is tetrabasic.

If the solution is further evaporated in a platinum vessel until white fumes begin to be given off, a transparent, glassy mass is obtained, which is the *glacial* phosphoric acid of commerce, or *meta-phosphoric acid.* Its formula is H_2O, P_2O_5 or HPO_3, and it is monobasic. Metaphosphoric acid will coagulate the albumen found in the white of egg, and will give a white, gelatinous precipitate of $AgPO_3$ when it is added to silver nitrate.

The other phosphoric acids do not coagulate albumen, nor do they precipitate silver nitrate. If, however, a few drops of soda be added to their solutions, the pyrophosphate which is formed will precipitate as white pyrophosphate of silver, $Ag_4P_2O_7$; the orthophosphate, as yellow orthophosphate of silver, Ag_3PO_4.

Metaphosphoric acid forms but one class of salts; but both the ortho- and pyro-phosphoric acids form a great variety of salts, inasmuch as their hydrogen may be replaced by one or more metals, in accordance with their atomicity,—a monad metal replacing one hydrogen atom; a dyad, two, etc.

Exp. 151.—Take the solution of superphosphate of lime, prepared by treating bone ash with sulphuric acid, and add sodium carbonate until the liquid is faintly alkaline. Filter off the calcium carbonate which forms, and evaporate the solution till a drop of it

placed on a watch glass readily crystallizes. On cooling the solution, crystals of di-sodium phosphate will form: $Na_2HPO_4, 12H_2O$.

Exp. 152.—Mix a portion of the preceding solution with caustic soda, and evaporate as before. The crystals formed are tri-sodium phosphate: $Na_3PO_4, 12H_2O$.

Exp. 153.—Mix another portion with orthophosphoric acid until it no longer precipitates calcium chloride, and then evaporate. On evaporation, crystals of monosodium phosphate, NaH_2PO_4, H_2O, are formed. All these salts give, with silver nitrate, the same precipitate of Ag_3PO_4.

243. If these three sodium salts be heated until they become dry, the water of crystallization will be expelled.

On heating them to redness, the first will lose a molecule of water and become sodium pyrophosphate.

$$2(Na_2HPO_4) \text{ ignited} = Na_4P_2O_7 + H_2O.$$

The second will suffer no further change; the third will lose two molecules of water and become sodium metaphosphate.

$$NaH_2PO_4 \text{ ignited} = NaPO_3 + H_2O.$$

If these residues are again dissolved in cold water, and a solution of silver nitrate added, they will yield: (1) white $Ag_4P_2O_7$, (2) yellow Ag_3PO_4, (3) white, gelatinous $AgPO_3$—showing the production in the first of pyrophosphoric acid, in the third of metaphosphoric acid: the orthophosphoric acid of the second remaining unaltered, because no part of its base was volatile.

If these silver precipitates be suspended in water, and a stream of hydrogen sulphide be passed through the liquid, black, insoluble silver sulphide will be formed, and the solutions of the different phosphoric acids may be obtained.

The meta- and pyro-phosphoric acids are converted into the orthophosphoric acids by prolonged boiling with water.

244. Tests. Orthophosphoric acid is estimated by adding to its solution a mixture of magnesium chloride, ammonium chloride, and ammonia. There precipitates white Mg'', NH_4PO_4, which becomes, on ignition, $Mg_2P_2O_7$. The acids are distinguished from one another by their reactions with silver nitrate and albumen.

245. Uses. Phosphoric acid is used in calico printing. The superphosphate of lime is used as a fertilizer.

Arsenic.

246. Arsenic is found native; in combination with sulphur, as realgar, As_2S_2, and orpiment, As_2S_3; but more frequently in combination with the metals, as arsenides. The chief sources of arsenic and its compounds are iron arsenide, $FeAs_2$, and arsenical pyrites, FeS_2FeAs_2. It is widely diffused, being found in small quantity in many metallic sulphides and the products obtained from them.

247. Preparation. The element arsenic is obtained from arsenical pyrites by roasting it in horizontal tubes. The arsenic is volatilized, and is then condensed in the cooler portions of the tubes. It is also obtained by heating arsenious anhydride with charcoal. This process may be illustrated by one of the methods employed in testing.

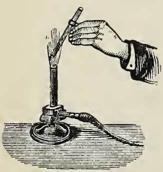

Fig. 72.

Exp. 154.—Introduce into a small tube of hard glass a little dry arsenious oxide, and place above this a few splinters of charcoal. First heat the coal to ignition, and then the arsenious oxide. As its vapor passes through the coal it is reduced, and condenses as a shining black ring on the colder portion of the tube.

248. Physical properties. Arsenic is a brittle solid of a steel-gray color and metallic luster. It volatilizes without fusing, at 180° C., and emits a peculiar, garlic-like odor. Its vapor density is double its atomic weight, and hence, like phosphorus, its molecule contains four atoms.

249. Chemical properties. Arsenic oxidizes in moist air, especially when heated. At a red heat it burns with a bluish white flame, and evolves white clouds of arsenious oxide. It is spontaneously combustible in chlorine, and combines readily with bromine, iodine, and sulphur.

When powdered arsenic is exposed to the air it forms a black powder which is sold under the name of *cobalt*, or "fly poison." All the compounds of arsenic are irritant poisons. The best antidote is prepared by precipitating ferric chloride with caustic magnesia.

250. Arsenetted hydrogen, H_3As, derives its chief interest from the fact that its production allows the detection of any soluble form of arsenic, even in very minute quantities. It is a colorless, coercible gas: sp. gr. 2.7. It has an alliaceous odor, and, even when largely diluted, is exceedingly poisonous.

251. Chemical properties. It burns in the air with a livid flame, producing arsenious anhydride and water. It is decomposed at a red heat into hydrogen and arsenic. When passed into a solution of silver nitrate, it precipitates metallic silver and forms arsenious acid. $6AgNO_3 + H_3As + 3H_2O = 6\underline{Ag} + 6HNO_3 + H_3AsO_3$.

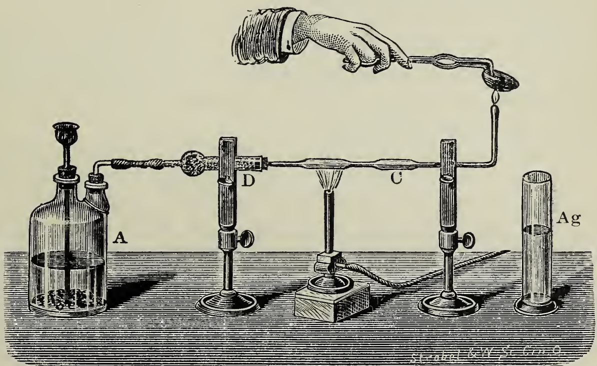

FIG. 73.

252. Marsh's test for arsenic is conveniently applied by the apparatus shown in Fig. 73.

Exp. 155.—A is a two-necked bottle; D, a drying tube containing potassium hydrate and calcium chloride; C, a tube of hard

glass contracted at one or two points and terminating in a vertical jet; Ag, a solution of silver nitrate.

To study the properties of the gas, let a handful of granulated zinc be put in the bottle and then covered with dilute sulphuric acid. After the air has been expelled from the apparatus, the jet of hydrogen may be lighted. It should burn with an almost colorless flame.

Now pour a little of a solution of arsenious acid in boiling water down the funnel tube. Notice, (1) the burning jet will change its color to a bluish white; (2) a cold porcelain plate held in the flame will acquire a dark, metallic spot; (3) obtain several of these, and, while doing so, heat the tube, C, in one or more places by the full flame of a good lamp. The white color will disappear from the burning jet, and a ring of metallic arsenic be formed in the tube a little beyond the flame of the lamp. Little or no deposit will then be formed on the plate. (4) Again remove the lamp and turn the jet into the silver solution. Black, metallic silver will be precipitated. The silver solution should be quite dilute at first, and, if much arsenic is present, more silver nitrate added from time to time.

To understand these reactions, we may suppose the arsenious acid to have been reduced by the nascent hydrogen to arsenic. A part of this remains as a black deposit on the zinc, and another part combines with another portion of the hydrogen, and escapes as arsenetted hydrogen. The white fumes which color the flame are arsenious acid. The black deposits are arsenic, produced by its decomposition. The silver solution will contain arsenious acid in the presence of free nitric acid.

We may now apply confirmatory tests. To the spots on porcelain, (1) add a fresh solution of an alkaline hypochlorite—the spots will disappear: (2) add ammonium sulphide—it will very slowly change to yellow arsenious sulphide. Now make several closed tubes of the tube, C. (3) Heat one of these tubes, and notice that the ring may be driven from one part to another. (4) Add a little nitric acid—the black ring will be dissolved. Apply any of the tests for arsenic acid to the solution. (5) Filter the silver solution, and carefully add just enough ammonia to neutralize the free nitric acid. If any undecomposed silver nitrate remains, a yellow precipitate of silver arsenite, Ag_3AsO_3, will form; or it will form on the addition of more silver nitrate.* Finally, try **Exp. 156.**

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* A more expeditious method consists in the substitution of sodium amalgam for the zinc: no acid is required. Slips of paper moistened with silver nitrate, and held over the gas which escapes, will blacken if only $\frac{1}{100000}$ grain of arsenic is present.

253. If all of these tests can be obtained, there can be little doubt of the presence of arsenic. In toxicological examinations others must also be had. So, also, the materials used must be tested, to determine that no arsenic is present in them.

This is done by subjecting the hydrogen which is at first evolved to the same tests for at least fifteen minutes before adding the suspected substances. It should be added that these substances must be previously freed from organic matters. If the liquid contains free nitric acid, a solid arsenetted hydrogen, H_2As, is formed in the flask.

254. The oxygen compounds of arsenic. Arsenic yields two anhydrides and a series of acids, which correspond to phosphorous and phosphoric acids.

ANHYDRIDES.		ACIDS.	
Arsenious anhydride,	As_2O_3.	Arsenious acid,	$H_3As\ O_3$
Arsenic anhydride,	As_2O_5.	Ortho-arsenic acid,	$H_3As\ O_4$.
		Pyro-arsenic acid,	$H_4As_2O_7$.
		Meta-arsenic acid,	$H\ As\ O_3$.

255. Arsenious anhydride, As_2O_3, is formed when arsenic is burned in air. It is prepared in large quantities by roasting arsenical pyrites in muffle furnaces through which the air is allowed to pass, and is condensed as a fine, white powder in large chambers.

Exp. 156.—Heat the arsenical deposit in a portion of the tube, C (Fig. 73), leaving both ends open to admit air. The black ring will volatilize and again condense to white, crystalline As_2O_3.

256. Physical properties. Arsenious anhydride is a white, tasteless solid: sp. gr. 3.7. The powder which is sold under the name of white arsenic, or ratsbane, is its usual form; but it can also be obtained by fusion as a glassy mass, which soon becomes opaque like porcelain. By boiling for several hours, 100 parts of water can dissolve 11.5 parts of the anhydride. The solution, on cooling, deposits 9 parts as octahedral crystals, leaving

2.5 parts dissolved. It is rather more soluble in hydrochloric acid; but, *on boiling with hydrochloric acid, arsenious chloride, $AsCl_3$, is formed and volatilizes.*

257. Chemical properties. No definite hydrate of the acid has been obtained. It forms, however, with the metals, well marked arsenites. Fowler's solution is potassium arsenite, made by boiling the anhydride in a solution of potassium carbonate. Arsenious acid acts as a reducing agent when heated with nitric acid and other bodies rich in oxygen, and is itself converted to arsenic acid, As_2O_5. If heated with charcoal, phosphorus, and similar reducing agents, it is reduced to the element arsenic, and acts as an oxidizing agent.

258. Uses. As an oxidizing agent, it is used in the manufacture of glass to convert ferrous to ferric oxide. It is also used in the manufacture of shot and of several green pigments. An arsenical soap, containing arsenious acid and camphor, is used by naturalists for preserving the skins of animals.

Tests.—Neutral solutions of the alkaline arsenites give a green precipitate (Scheele's green) with cupric sulphate, and a yellow precipitate with silver nitrate.

Reinsch's test is made by acidulating the acid or its compounds with hydrochloric acid, and heating the mixture gently after the addition of a bright copper strip. After a little while, a steel-gray coating of Cu_5As_2 is formed.

259. Physiological properties. Although two decigrammes of arsenious acid are sufficient to destroy life, it is possible gradually to accustom the human body to daily doses of three decigrammes, or even more. As a medicine, small doses of arsenious acid are used in intermittent fevers and in skin diseases.

260. Arsenic acid is prepared by oxidizing arsenious anhydride with nitric acid. On evaporating the solution

to a syrup, deliquescent crystals of $3H_2O, As_2O_5 + H_2O$ are deposited in rhomboidal laminæ. These crystals, heated to 100° C., lose the water of crystallization and become the tribasic acid ($3H_2O, As_2O_5$): at 160° C., pyro-arsenic acid ($2H_2O, As_2O_5$); at 260° C., meta-arsenic acid (H_2O, As_2O_5); at a dull red heat, arsenic anhydride (As_2O_5), which decomposes at a full red heat. All these bodies dissolve in water and yield the trihydrate.

261. Properties. Arsenic acid appears to be less poisonous than arsenious acid, but its acid properties are more marked. It is largely used in calico printing and in the manufacture of aniline colors.

Tests.—Arsenic acid yields a brick-red silver arseniate, Ag_3AsO_4, with silver nitrate. It forms many precipitates which closely resemble those of the tribasic phosphoric acid. The ammonio-magnesian mixture gives white $Mg''NH_4AsO_4$, which is used for the quantitative determination of arsenic.

Arsenic acid and its salts are reduced by boiling with sulphurous acid. They then yield the tests for arsenious acid.

All compounds of arsenic in acid solutions yield, with sulphuretted hydrogen, a yellow precipitate of As_2S_3; but it must be noted that with the higher compounds the precipitate forms slowly, and generally only after heating.

262. The principal sulphides of arsenic are realgar, or red orpiment, As_2S_2; yellow orpiment, or king's yellow, As_2S_3; and the penta-sulphide, As_2S_5. The first two are found native, but all are prepared artificially.

Realgar is used in pyrotechny. One part of realgar mixed with 3.5 parts of sulphur and 14 of saltpeter yields a beautiful white flame (Indian fire).

The other two are interesting because they form soluble compounds with the alkaline sulphides. These compounds are sulpho-salts which are analogous to the oxy-salts, and, hence, As_2S_3 is sometimes called sulpharsenious acid, and As_2S_5, sulpharsenic acid.

Sulpharsenious acid is the yellow precipitate formed by passing H_2S into an acidified solution of the arsenites. The same compound mixed with free sulphur is formed by treating arsenic acid with H_2S. It forms slowly in cold solutions; more rapidly on boiling.

If, however, sodium arseniate is saturated with H_2S, a soluble sulpharseniate of sodium, $2Na_2S, As_2S_5$, forms. Hydrochloric acid added to this solution precipitates the yellow As_2S_5.

Either of these sulpho-acids is soluble in ammonium carbonate.

Antimony.

263. Antimony is found native, but generally in combination with oxygen, sulphur, and certain metals.

264. Preparation. The antimony of commerce is obtained from stibnite, Sb_2S_3, by fusing it with scrap iron: $Sb_2S_3 + 3Fe = 3FeS + 2Sb$. The product is crude antimony, which is purified by a second fusion with sodium carbonate. Pure antimony may be obtained for experimental purposes by heating tartar emetic to bright redness in a covered crucible.

265. Physical properties. Antimony is a brittle, crystalline metal of lustrous, bluish white color: sp. gr. 6.7. It melts at 450° C., and volatilizes at red heat. The antimony which is obtained by electrolysis sometimes has the curious property of exploding when heated or struck.

266. Chemical properties. Antimony is not oxidized in air at ordinary temperatures, but, when heated above its melting point, oxidizes rapidly, and, at a red heat, burns with a white flame.

Exp. 157.—Heat a lump of the *pure* metal on charcoal before the blowpipe. Dense, white fumes will be given off. These are antimonious oxide, Sb_2O_3. Allow the molten mass to cool before it is completely burnt away. It will become covered with a crystalline network of the same oxide.

267. Uses. Antimony forms alloys with most of the heavy metals, rendering them harder, more brittle, and frequently suitable for forming sharp casts. Among these are type metal (Sb and Pb), Brittania metal, and pewter (Sn and Sb).

268. The compounds of antimony.—(I) **The chlorides.** Finely powdered antimony takes fire spontaneously in chlorine gas, forming either $SbCl_3$ or $SbCl_5$, according as the antimony or chlorine is in excess. Hence, if a slow current of chlorine be passed through a tube containing antimony, antimonious chloride, $SbCl_3$, will be formed. This condenses as a soft, gray solid known as the butter of antimony. It is also formed when antimonious sulphide is boiled with hydrochloric acid.

If chlorine gas be passed over antimonious chloride, a yellowish, volatile liquid forms, which is antimonic chloride, $SbCl_5$.

(II) **Oxides.** Both of these chlorides are decomposed when added to a large quantity of water. The first yields a white powder, the oxychloride of antimony ($SbCl_3, Sb_2O_3$); the second, white metantimonic acid ($2H_2O, Sb_2O_5$). If these two precipitates are gently heated, they form antimonious oxide, Sb_2O_3, and antimonic oxide, Sb_2O_5. When either of these is strongly heated, a yellow powder is formed which is probably a mixture of both: $Sb_2O_3, Sb_2O_5 = 2Sb_2O_4$.

(III) **Acids.** These oxides of antimony dissolve in alkaline solutions to form antimonites and antimonates. They may also be obtained as antimonious acid, $H_2O, Sb_2O_3 = HSbO_2$, and antimonic acid, $H_2O, Sb_2O_5 = 2(HSbO_3)$. This last corresponds to metaphosphoric acid. There is also a tetrabasic acid, $H_4Sb_2O_7$, which is called metantimonic acid. It corresponds to pyrophosphoric acid. Potassium metantimoniate is sometimes used in testing for sodium.

269. Antimonious oxide acts not merely as an acid, but also as a basic anhydride. It readily dissolves in tartaric acid to form antimonious tartrate. It also dissolves readily in acid potassium tartrate, and thereby forms the well-known tartar emetic:

$$Sb_2O_3 \text{ or } (SbO)_2O + 2(KH, C_4H_4O_6) = 2(K, SbO, C_4H_4O_6) + H_2O.$$

In these cases we may suppose it to be represented by the radical antimonyl $(SbO)'$.

270. Tests. When a stream of hydrogen sulphide is passed through acidulated solutions containing the compounds of antimony, sulphides of antimony are formed which are sulpho-acids similar to those of arsenic. The antimonic compounds yield a yellowish red antimonic sulphide, Sb_2S_5; the antimonious compounds, orange red antimonious sulphide, Sb_2S_3, soluble in ammonium sulphide. Both of these dissolve in hot hydrochloric acid as chlorides, which are decomposed by a large quantity of water—$SbCl_5$ yielding $H_4Sb_2O_7$; $SbCl_3$, a white oxychloride, $SbCl_3$, Sb_2O_3, or $3SbOCl$, soluble in tartaric acid.

Marsh's test yields, with the compounds of antimony, an odorless, antimonetted hydrogen, H_3Sb, which gives reactions similar to those observed with arsenic. They are, however, easily distinguished. (1) The metallic deposits are darker and are less volatile than those of arsenic. (2) They are insoluble in alkaline hypochlorites which do not contain free chlorine. (3) Gently warmed with nitric acid, they are oxidized but not dissolved. The antimonious oxide formed yields black Ag_4O, with neutral silver nitrate and ammonia. (4) They are readily soluble in ammonium sulphide. (5) The deposit in the silver solution is black Ag_3Sb, silver antimonide; hence, if any precipitate forms in the solution when filtered on the addition of ammonia, it is the oxide of silver.

Reinsch's test yields purple copper antimonide.

271. Uses. Antimonious chloride is used for bronzing gun barrels. Antimonious sulphide is used in the preparation of blue signal lights (Bengal light). Tartar emetic is used in medicine.

Bismuth.

272. Bismuth is found chiefly in the metallic state, and is freed from its earthy impurities by heating the ore in iron cylinders which are fixed in an inclined position over a furnace. (Fig. 74). The bismuth melts at 264° C., and runs out at the lower ends of the tubes into iron vessels.

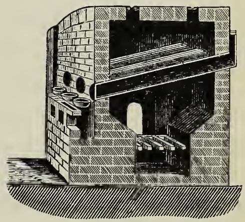

Fig. 74.

273. Physical properties. Bismuth is a brittle metal of a reddish luster: sp. gr. 9.8. It may be obtained in beautiful, rhombohedral crystals by melting several pounds of it, allowing it to cool till a crust has formed on its surface, and then pouring out the metal which still remains molten. The crystals will be found lining the interior of the crucible. The metal expands $\frac{1}{32}$ in solidifying. It is the most highly dia-magnetic substance known.

274. Chemical properties. Bismuth does not oxidize in the air at ordinary temperatures. It burns when strongly heated in the air with a bluish flame, forming yellow fumes of bismuthous oxide, Bi_2O_3. It unites directly with chlorine, bromine, iodine, and sulphur. It readily dissolves in nitric acid, forming the bismuthous nitrate, $Bi_2O_3, 3N_2O_5$ or $Bi(NO_3)_3$.

275. Uses. Bismuth is used, together with antimony, in the construction of thermo-electric batteries. Its presence in alloys has a wonderful influence in lowering the melting point. Rose's fusible metal melts at 94° C. It is composed of two parts of bismuth and one each of lead and tin, or very nearly Bi_2PbSn_4. This is valuable for taking impressions of dies, inasmuch as it expands on cooling, and reproduces the faintest lines with accuracy.

276. The compounds of bismuth.—(I) **Oxides.** If bismuthous nitrate is dissolved in a small quantity of water, and added to an excess of potassium hydrate, bismuthous hydrate precipitates as $3H_2O, Bi_2O_3$ or H_3BiO_3. This body becomes, on ignition, Bi_2O_3, bismuthous oxide. It seems also to enter into compounds as the monatomic radical $(BiO)'$, to form salts which are known as basic or sub-salts.

Bismuthic acid, H_2O, Bi_2O_5 or $HBiO_3$, is formed by passing chlorine gas through a hot potash solution which contains bismuthous hydrate in suspension. Its acid powers are weak and its salts are of no importance.

If bismuthous nitrate is thrown into a large quantity of water, it precipitates a basic or sub-nitrate of bismuth, Bi_2O_3, N_2O_5 or $(BiO)'NO_3$, also known as flake white.

(II) **Chlorides.** If the nitrate is poured into a solution of sodium chloride, an oxychloride of bismuth, $BiCl_3, Bi_2O_3 = 3BiOCl$, or "pearl white," precipitates. This dissolves in hydrochloric acid to bismuthous chloride, $BiCl_3$, and again precipitates on the addition of water. The formation of these basic bodies by water is characteristic of bismuth. Unlike the similar compounds of antimony, they are insoluble in tartaric acid.

(III) **Salts.** Bismuthous carbonate, $(BiO)_2CO_3$, is formed by decomposing bismuthous nitrate by an excess of an alkaline carbonate. This salt and the basic nitrate are used in medicine. Pearl white is used as a cosmetic.

Tests.—The salts of bismuth are sufficiently characterized by their decomposition with water. They form, with soluble sulphides, black precipitates which are bismuthous sulphide, Bi_2S_3.

Recapitulation.

Review sections 190, 191, and 193.

This group contains all the pentad elements. Although the members of the group exhibit marked differences, they also exhibit

a marked gradation of properties, which will be best shown by dividing them into sub-groups, as follows:

I	II	III	IV	V
N 14	P 31	P 31	P 31	As 75
P 31	V 51	As 75	Sb 122	Sb 122
V 51	As 75	Sb 122	Bi 210	Bi 210

Note that the atomic weight of the middle element in each of these sub groups is very nearly the mean of the other two. In each of these sub-groups the middle element also exhibits more or less resemblance to the first and third, and may be said, in a general sense, to form a connecting link between them.

Among the numerous points to be noticed are:

(1) Nitrogen is generally a gas; phosphorus, a vitreous solid; and vanadium, a semi-metal. The nitrogen compounds are easily decomposed; the phosphorus compounds are exceedingly pliant, changing readily from one form to another. These qualities fit them for the laboratory of nature, and we find them necessary both to vegetables and animals.

(2) The pentoxides of the second sub-group yield ortho-, pyro-, and meta- "ic" acids, which form "ate" salts that are isomorphous and generally agree in their properties.

(3) The elements of the third sub-group are either poisonous (P) or form poisonous compounds (As and Sb). Sb alone forms no ortho-, oxy-acid. The molecule of P and of As contains 4 atoms; that of Sb has not been determined.

(4) The oxides of the fourth sub-group form a decreasing series as regards their acid properties. Those of P are generally acid anhydrides; Sb_2O_3 is either acid or basic; Sb_2O_5, acid; Bi_2O_3, basic; and Bi_2O_5, feebly acid.

(5) The sulphides of the fifth sub-group are all sulpho-anhydrides, which form with sulphides of many metals sulpho-salts analogous to the oxy-salts.

The formula of the chloride of nitrogen is unknown. All the terchlorides of the remaining elements are decomposed by water, forming generally oxy-chlorides of the formula (RO) Cl. (See also § 212). Imagine in these compounds the chlorine to be removed; there will remain a monatomic radical of the formula $(R'''O'')'$, which is represented in $(SbO)'$, $(AsO)'$, and probably by $(BiO)'$ in basic bismuthous compounds.

CHAPTER VIII.

BORON.

Symbol, B. Atomic weight, 11. Specific gravity, 2.68. Melts about 300° C. Isolated by Gay-Lussac in 1808.

277. Boron is a triad element which derives its chief importance from boracic or boric acid, H_2O, B_2O_3 or HBO_2.

Borax ($Na_2O, 2B_2O_3, 10H_2O$ or $Na_2B_4O_7, 10H_2O$) is found native as tincal in certain lakes of Asia and California. Boric acid is found native as sassolite. It is principally obtained from the volcanic districts of Tuscany.

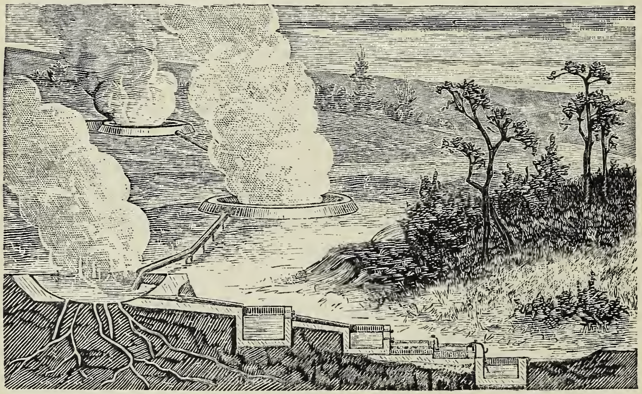

FIG. 75.

In that country numerous jets of steam, called *suffoni*, issue from fissures in the ground, and are condensed into natural or artificial ponds called lagunes. The water in these lagunes contains dilute boric acid; and, on evaporation, which is carried on by the natural

heat of the suffoni, yield a crude boric acid. This is either purified by re-crystallization or is employed in the manufacture of borax. Pure boric acid may be obtained from borax.

Exp. 158.—Boil 3 parts of borax in 12 of water, and to the hot solution, filtered if necessary, add 1 part of strong sulphuric acid. On cooling, boric acid separates in white, pearly looking scales, unctuous to the touch. These are the orthoboric acid, $3H_2O, B_2O_3$. When heated, they are converted to pyroboric acid, $H_2B_4O_7$; then to metaboric acid, HBO_2; and finally to the anhydride B_2O_3, which fuses to a transparent glass.

278. Boric acid is soluble in 25 parts of water at 18° C., and in 3 parts at 100° C. It must be reckoned as a feeble acid: its solution colors litmus a dark wine red, and turmeric a brown red. At high temperatures, fused boric acid, and also borax, dissolves many metallic oxides to form transparent glassy borates. Hence they are employed as fluxes in soldering, and are often added to enamels to render them more fusible. Large quantities of borax are used in glazing stone-ware.

Exp. 159.—Bend the end of a thin platinum wire into a small loop. Heat this and touch it to a small fragment of dried borax. The borax will adhere to the wire. Now introduce the borax into the flame of a Bunsen's lamp. It will fuse to a clear glassy bead.

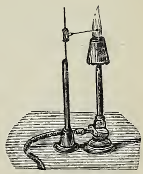

FIG. 76.

Very small quantities of several of the metallic oxides produce characteristic colors when they are added to the borax bead, and hence these beads are often used in blowpipe testing.

Exp. 160.—Just touch the borax bead with cobalt nitrate; then melt the bead again. It will become a beautiful blue. Manganese gives an amethyst bead in an oxidizing flame; chromium and copper, a green bead; ferric oxide gives a greenish yellow bead. Many oxides, like those of silver, nickel, and lead, yield grayish beads in the reducing flame, owing to the presence of the reduced metal.

279. Test. Boric acid is detected by its imparting a a green color to flames.

Exp. 161.—(I) Dissolve a little boric acid in alcohol, and ignite. A beautiful green flame is produced, which, when examined by the spectroscope, is resolved into a series of five green bands.
(II) Form a borax bead on a platinum wire; then moisten it with strong sulphuric acid. On bringing this into a colorless flame, the green flame characteristic of boron will be produced.

280. Boron may be obtained as an amorphous, brown powder by heating vitrified boric anhydride with sodium. It has also been obtained as graphitoidal boron in brilliant scales, like graphite, and as adamantine boron in brilliant, highly refracting crystals which resemble the diamond both in their luster and hardness. These latter are thought to be allotropic forms of boron; but the adamantine always contains carbon, and the graphitoidal, aluminum.

Its physical properties strongly resemble those of carbon and silicon, with which it was formerly classed. All form feeble acids by direct union with oxygen, whose salts also frequently resemble each other. Their relationship may be expressed graphically thus:

$$\begin{array}{ccc} B'''11 & & C^{IV}12 \\ & \searrow \quad \swarrow & \\ & Si^{IV}28 & \end{array}$$

Recapitulation.

Boron is the only triad in the list of the non-metals.
Its principal salt is borax.

CHAPTER IX.

THE CARBON GROUP.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C	DISCOVERER.
Carbon	C	12	3.33		
Silicon	Si	28	2.49		Berzelius, 1823.
Titanium	Ti	50	5.3?		Gregor, 1791.
Zirconium	Zr	89.6	4.15		Klaproth, 1789.
Tin	Sn	118	7.29	230°	

281. This is a group of tetrad elements. All of them unite with four atoms of chlorine to form tetrachlorides. Carbon and silicon form gaseous, inflammable compounds with four atoms of hydrogen, as CH_4; SiH_4. All of the elements in this group form dioxides and disulphides, which unite as acids with the alkaline oxides and sulphides to form oxy- and sulpho-salts, as K_2O, CO_2; K_2S, CS_2; or K_2CO_3 and K_2CS_3.

Carbon and tin also act as dyads in a few compounds; as CO, $SnCl_2$, SnO, SnS. These compounds are either indifferent bodies, or they possess feebly basic properties.

Carbon and silicon are non-metals whose physical properties resemble those of the triad element boron. One of their allotropic conditions, the graphitoidal, has some of the physical characters of the metals, viz, their luster and the property of conducting heat and electricity.

Zirconium, titanium, and tin are semi-metals very closely resembling each other, and are allied in their physical properties to the metals.

282. Carbon is remarkable for the great number of its hydrogen compounds. These are spoken of collectively as the *hydrocarbons*, and include the greater number of the essential oils, coal oils, and the gases used for illumination. They are generally classed together and studied in *organic chemistry*, which may be defined as the "chemistry of the carbon compounds." Only the oxides and sulphides will be presented in this chapter.

Carbon.

283. Carbon is one of the most abundant elements. In combination it is an essential constituent of all organic substances; of all carbonates, such as limestone, and is found in the air in carbonic anhydride. In the free state it occurs in three allotropic forms: (1) pure in the diamond; (2) nearly pure in graphite; and (3) less pure in anthracite coal. Carbonado, gas carbon, coke, lampblack, and charcoal are varieties of these. Bituminous coal, asphalt, and jet contain also hydrocarbons which are volatilizable by heat.

Physical Properties of Carbon.

284. (I) **The diamond occurs** as small, rounded bodies in the detritus of certain quartzose rocks which are found principally in Golconda, Brazil, and South Africa. Its crystalline form is that of the octahedron: sp. gr. 3.5. It has a brilliant luster, which is increased by cutting so as to furnish numerous facets capable of reflecting and refracting light in various directions. It is the hardest substance known, and hence can be cut only by means of dust obtained by pounding up the least valuable sorts of diamonds. When broken, the diamond

naturally cleaves in directions nearly parallel to other faces of the octahedron, but generally in faces more or less curved. These curved faces intersect in curved edges, which are more suitable than straight edges for cutting glass, as they are capable of penetrating the glass like a wedge, instead of merely scratching its surface.

The *carbonado*, a black diamond found in Brazil, has lately been employed in rock cutting to great advantage.

285. (II) **Graphite** is occasionally found in six-sided plates which belong to the rhombohedral system. It generally occurs in the amorphous state, and is known as plumbago or black lead: sp. gr. 2.2. Graphite has a dark, steel-gray color, a semi-metallic luster, and is unctuous to the touch. It is found generally in the older rocks, and occurs most abundantly in Ceylon, Siberia, and California. The graphites of Cumberland, England, and of Ticonderoga, N. Y., are especially noted for their purity. Some varieties of cast iron contain so much graphite that it separates in the crystalline form (*kish*) when the molten iron is slowly cooled.

Graphite is used for making lead-pencils and crucibles, for polishing stoves, and as a lubricant to diminish the friction of machinery. It is a conductor of electricity, and is used in the electrotype process to impart a conducting surface to non-conducting materials, such as wax.

286. (III) **Mineral coal exists** in three principal varieties: anthracite, bituminous, and lignite. These are all undoubtedly of vegetable origin; and it is possible to form a series beginning with peat, in which much of the material is not thoroughly carbonized; through lignite, in which the woody structure is clearly apparent; cannel coal, from which large quantities of the so-called coal oils may be distilled; bituminous coal, which readily cakes together when heated, and burns with a

bright blaze; non-caking bituminous coal; anthracite coal, which contains 90 per cent of carbon; to the coals of Greenland, which are sometimes regarded as graphite.

287. (IV) **Bituminous coals,** when distilled, yield a large number of volatile hydrocarbons, and a porous, often brilliant looking solid, which is known as *coke.* It is an accidental product in the manufacture of illuminating gas, but is also purposely prepared for iron smelting, to obtain a fuel that does not cake in burning.

Another very dense and hard form of carbon, which is slowly produced in gas retorts by the decomposition of the volatile hydrocarbons; is known as gas carbon. It is used as the negative element in many forms of galvanic batteries. The carbon plates are usually prepared by compressing a mixture of coke, coal, and treacle in iron moulds, and then strongly heating the mixture.

288. (V) **The imperfect combustion** of organic substances also yields various forms of carbon. Wood charcoal is generally made by piling billets of wood in large heaps, which are covered with turf,—holes being left at the bottom for the air to get in, and a flue left open at the middle of the heap. The heap is then kindled at the center, and, when the combustion is well established, the flue is closed and the mass is allowed to smoulder until the wood is perfectly carbonized. A better method consists in heating the wood in iron cylinders.

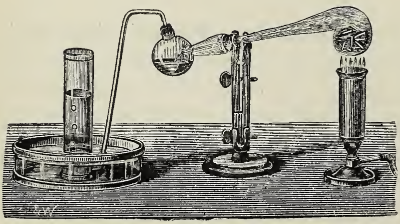

Fig. 77.

Exp. 162. — Place in a glass retort splinters of wood, and arrange the apparatus as shown in Fig. 77. On heating the retort, inflammable gases will collect in the cylinder over water; tar, water,

methylic alcohol, and acetic acid, in the receiver; and charcoal will remain in the retort.

The charcoal remaining weighs about one-fourth of the original wood. It retains the general structure of the wood, even to the concentric rings. Owing to its porous nature, it is capable of absorbing large amounts of gases; it absorbs 90 times its volume of ammonia, and 55 times its volume of sulphuretted hydrogen. Hence it is of great use in purifying drinking water, and as a deodorizer for putrefying matters. Those gases are best absorbed that are easily condensed, seeming to indicate that the absorbed gases assume in part a liquid condition.

Exp. 163.—Fill a long glass tube with dry ammonia over a trough containing mercury, and then introduce a fragment of charcoal recently ignited and cooled under mercury. In a short time the coal will so absorb the ammonia that the mercury will be forced up the tube. (Use apparatus in Fig. 1).

289. (VI) **Animal charcoal** is made by heating crushed bones in iron retorts. It is a mixture of very finely divided coal and calcium phosphate. It is largely used for decolorizing sugar syrups and in refining alcohol.

Exp. 164.—To show these properties, shake a handful of freshly ignited animal charcoal with an infusion of logwood: boil, and then filter the mixture through paper. The liquid will have lost its color.

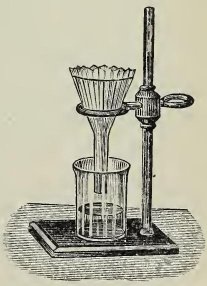

FIG. 78.

It is important to observe that in many cases other bodies than the coloring matters are retained by the charcoal. Thus, it removes the bitter principle of beer, and, what is more important, most of the alkaloids—as quinine and strychnine—from their solutions.

290. (VII) **Lampblack** is the soot obtained by the imperfect combustion of resinous, tarry, or oily matters, or of the natural gases of petroleum.

Exp. 165.—Set fire to a lump of resin, and hold a cold white plate over the flame. Abundance of soot will be deposited upon it.

If the first product is calcined in a covered crucible, a very nearly pure form of carbon is obtained. Its impurities, however, do not affect its employment as a pigment in the manufacture of paint, printing ink, and blacking.

All these forms of carbon are practically infusible, although it is stated that, at the exceedingly high temperature of the voltaic arc, phenomena have been observed which indicate its fusion and volatilization.

291. Chemical properties. At ordinary temperatures, all these forms of carbon are chemically inert. Manuscripts written with an ink made of lampblack, still perfectly legible, have been exhumed with Egyptian mummies. It is a common practice to char the ends of wooden stakes which are intended to be sunk in the ground, so that the interior may be protected from decay by a superficial coating of charcoal.

At high temperatures, carbon enters into direct combination with oxygen, sulphur, hydrogen, nitrogen, and a few of the metals. Porous wood charcoal ignites in the air at 240° C.; anthracite requires a much higher temperature; and the diamond, the highest temperature of all the forms of carbon. At very high temperatures, the affinity of carbon for oxygen is so great that it is capable of removing oxygen from its compounds with the metals. Hence, it is largely employed as a reducing agent by the metallurgist. (See Exp. 154).

Exp. 166.—Mix basic bismuthous nitrate with an equal bulk of charcoal in fine splinters, and heat this mixture in a crucible to ignition. (For apparatus, see Fig. 67). On cooling, a bead of metallic bismuth will be found in the crucible. A little decrepitated sodium chloride may be placed to advantage on the top of the crucible, so as to exclude the air.

Repeat this experiment with litharge.

Heated coal is even able to decompose water. Thus,

if steam be passed over red-hot charcoal (use apparatus in Fig. 7), the carbon will unite with its oxygen, liberating hydrogen and forming carbonous oxide and carbonic anhydride:

$$4H_2O + 3C = \widehat{CO_2} + 2\widehat{CO} + \widehat{H_8}.$$

292. The compounds of carbon and oxygen are carbonous oxide and carbonic anhydride. Both are aëriform bodies, formed by the direct union of the two elements when any form of carbon is burned in air. When the supply of air is abundant, nearly pure carbonic anhydride is produced; but when the supply is limited, it is mixed with carbonous oxide.

293. Carbonous oxide, CO, is more frequently known by the name of carbonic oxide. It may be prepared by gently heating thoroughly dried potassium ferrocyanide with four times its weight of sulphuric acid, and washing the gas with a solution of potassium hydrate. (Fig. 79). The lamp must be removed as soon as the gas begins to form rapidly.

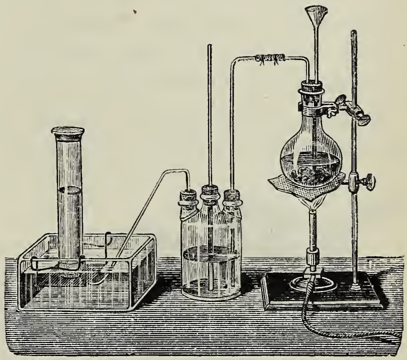

FIG. 79.

$$K_4Fe(CN)_6 + 6H_2O + 6(H_2SO_4) =$$
$$6\widehat{CO} + 2(K_2SO_4) + FeSO_4 + 3[(H_4N)_2SO_4)].$$

It is also produced by the reaction mentioned in § **292.**

294. Physical properties. Carbonous oxide is a permanent, colorless gas, nearly insoluble in water: sp. gr. 0.967. It is completely absorbed by a solution of cuprous chloride.

295. Chemical properties. Carbonous oxide burns in the air with a pale blue flame and forms carbonic anhydride, CO_2. Conversely, carbonic anhydride is readily reduced to carbonous oxide. Thus, when the air enters at the bottom of a clear fire, the oxygen at once unites with the carbon to form carbonic anhydride. As this gas passes through the heated embers above, it is reduced by the coals to carbonous oxide ($CO_2 + C = 2\widehat{CO}$). The blue flame which is noticed on the top of anthracite fires is produced by the combustion of this carbonous oxide in the fresh air above the coals.

Carbonous oxide is a reducing agent. It may be employed instead of hydrogen to reduce cupric or ferric oxide in the apparatus shown in Figs. 7 or 27.

The reactions already mentioned play an important part in many metallurgical operations.

Thus, in the reverberatory furnace represented in Fig. 80, the metallic oxides are placed on the hearth and the fuel at the side. The fuel is burned so as to yield carbonous oxide, which then plays over the hearth, abstracts the oxygen from the ores, and reduces them to the metallic state. The production of this oxide is increased by placing pans of water below the bars, so that steam may be formed and produce the reaction mentioned in § **292.**

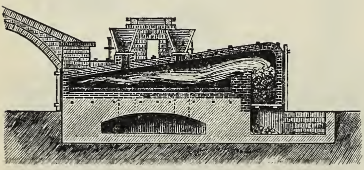

Fig. 80.

Carbonous oxide unites directly with chlorine, sulphur, and potassium, but it does not form salts with either acids or bases. It is regarded as the free state of the diatomic radical carbonyl, and enters as such into many organic compounds.

296. When carbonous oxide is passed over hot, moistened potassium hydrate, potassium formiate is produced: $KHO + CO = KHO, CO$; or KO, CHO; or $H, COOK$.

This is an interesting reaction, as from this salt formic acid, HO, CHO, may be prepared, an example of the *synthesis* of organic bodies from inorganic materials.

297. Physiological properties. Carbonous oxide is so poisonous that one per cent of it diffused through the air produces giddiness in those that breathe it, and, after a while, a fatal result through suffocation.

298. Carbonic anhydride, CO_2. We have already noticed that this body is produced by the complete combustion of carbon and of carbonous oxide. It is also produced by the processes of respiration, fermentation, and decay. As these processes are going on continually, enormous quantities of carbonic anhydride would accumulate in the air, were it not that the leaves of plants, under the influence of sunlight, decompose this gas, assimilating the carbon to form woody tissue and other vegetable products, and giving back the oxygen to the air. This so maintains the balance of nature that the average quantity of carbonic anhydride in the atmosphere is about one twenty-five hundredth part of the whole. Liquors like champagne and soda water owe their effervescing character to the carbonic acid which has been retained in them by pressure.

299. Preparation. Carbonic anhydride is usually prepared by the action of dilute acids upon the carbonates.

Exp. 167.—Place a few fragments of marble in a flask, and pour upon them dilute hydrochloric acid. The gas may be collected over water or by displacement. (Use apparatus in Fig. 20).

$$CaO, CO_2 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

300. Physical properties. Carbonic anhydride is a colorless, coercible gas, having a peculiar, pungent odor. Its specific gravity (1.529) is so great that it may be poured from one vessel to another (Fig. 81); and, consequently, its rate of diffusion is so small that it some-

times accumulates in wells and caverns. This is notably seen in the *Grotto del Cane*, near Naples.

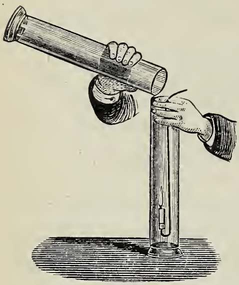

FIG. 81.

At ordinary temperatures, carbonic anhydride is condensed by a pressure of 50 atmospheres to a colorless liquid: sp. gr. 0.83. If this liquid anhydride is liberated from pressure, a portion rapidly volatilizes, and, by so doing, produces a cold of —77° C., which is sufficient to freeze the remaining portion into a snow-white, flocculent mass. This may be handled notwithstanding its low temperature, because it is kept from contact with the hand by a layer of the gas (spheroidal condition); but, if pressed into actual contact with the skin, it produces a blister like a burn. Wetted with ether, it easily solidifies mercury, and *in vacuo* produces a cold of —110° C.

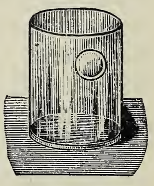

FIG. 82.

FIG. 83.

301. Chemical properties. Carbonic anhydride is incombustible, and extinguishes the flame of ordinary combustibles. Its high specific gravity and power of extinguishing flame may be illustrated by the following experiments.

Exp. 168.—An ordinary soap bubble will float on the surface of the gas. Evolve the gas in a broad-mouthed jar by placing marble chippings and acid at the bottom. (Fig. 82).

Exp. 169.—Balance a light paper box on an arm of a balance: the anhydride may be poured into the box and will depress the beam. (Fig. 83).

Exp. 170.—A lighted taper plunged into the gas will be extinguished. It may also be extinguished by pouring the gas upon it from some distance above. (Fig. 81).

Exp. 171.—The gas may be drawn up in buckets from the bottom of large jars and used as in Exps. 169 and 170. It may be reduced to carbonous oxide by ignited coals, and also by some metals, as Zn and Fe, at high temperatures.

Exp. 172.—Pass a dry stream of the gas over melted sodium. It is in part reduced to carbon, while another part combines with the sodium. (Fig, 82).

$3CO_2 + Na_4 = 2(Na_2O, CO_2) + C.$

The product formed in this case is the normal sodium carbonate, Na_2CO_3.

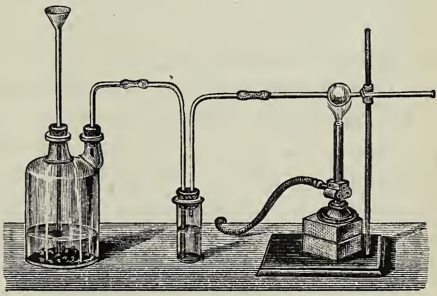

FIG. 84.

Potassium hydrate rapidly absorbs the gas, and may be used to separate it from mixtures with most other gases. When a large excess of the gas is passed into a solution of potassium hydrate, the product formed is $KHCO_3$, acid potassium carbonate, or bicarbonate of potassa. Similar salts are formed with the other metals. There are also sesquicarbonates which may be regarded as mixtures of the other two, as $2NaHCO_3 + Na_2CO_3 = Na_4H_2, 3CO_3$, and orthocarbonates like half-burned lime, $2CaO, CO_2$ or $Ca''_2 CO_4$.

The solution of the gas in water (§ **36**) is regarded as *carbonic acid*, but it has not been isolated. Its theoretical formula should be $C^{IV}(OH)_4$ or H_4CO_4, a tetrabasic ortho-acid. Generally speaking, it acts as a dibasic acid, having the formula H_2CO_3 or H_2O, CO_2.

Carbonic acid is a feeble acid that is easily displaced by almost all other acids. All the carbonates, except those of the alkalies, are decomposed by heat. These are decomposed when boiled with calcium hydrate.

302. Physiological properties. Carbonic acid is not poisonous when taken into the stomach, but the gas acts injuriously when breathed, except when exceedingly dilute. Fatal accidents have occurred from the accumulation of this gas in old cisterns, brewers' vats, and in mines, where it is known by the name of "choke damp." Air containing one per cent of carbonic anhydride produces in most persons languor and headache; a larger proportion causes stupor; and nine per cent is sufficient to cause suffocation and death.

The air expired from the lungs contains about four per cent of the gas. Air which has been twice respired contains enough of the gas to extinguish a taper. A full-sized man evolves from his lungs and skin about 0.7 cubic foot per hour of carbonic anhydride. In order that he may continue to breathe without inconvenience, it is necessary that this evolved gas should be distributed through at least 140 cubic feet of fresh air, so that it may not exceed one-half of one per cent of the air. Hence, there is a necessity for abundant ventilation of occupied apartments. It should be remembered that lamps also produce carbonic acid. A gas burner consuming six feet of gas per hour evolves as much carbonic acid as one man.

303. Uses. Carbonic anhydride has proved of great service in extinguishing fires in coal mines; and several devices have been proposed by which it may be turned to account in extinguishing ordinary conflagrations. Water containing carbonic acid is of great importance in the chemistry of Nature. It is capable of dissolving calcium carbonate and other bodies not soluble in pure water, and thus assists in disintegrating rocks and pre-

paring soils for the uses of plants. The gas is also used in manufacturing various carbonates, as those of sodium and lead.

304. Tests. Free carbonic anhydride may be recognized by passing it into lime-water (Fig. 5), when it causes a precipitate of calcium carbonate.

Exp. 173.—The presence of this gas in expired air may readily be shown by blowing a deep breath into lime-water. (Fig. 85).

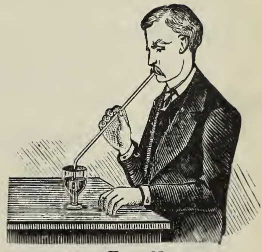

Fig. 85.

Exp. 174.—The carbonic anhydride in air may be shown by the following apparatus. A wide tube, a foot long, is placed in an inclined position, and is fitted at both ends with vertical tubes. It is then half-filled with lime-water. The air slowly drawn through this by means of an aspirator renders the lime-water milky. The aspirator may consist of a large can furnished with a siphon, as shown in Fig. 86.

The carbonates are known by their effervescing and by evolving CO_2 when a strong acid is poured upon them.

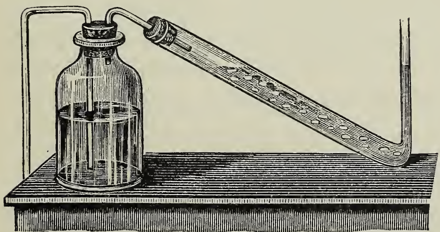

Fig. 86.

305. Carbonic disulphide, CS_2, is prepared by passing the vapor of sulphur over coke or charcoal heated to redness. It is frequently present as one of the most injurious impurities in coal gas.

306. Physical properties. Carbonic disulphide is a colorless, diathermanous liquid of high refracting powers (1.645), and, when pure, of not unpleasant odor: sp. gr. 1.27. Usually, however, the odor of its vapor is very

offensive. It volatilizes rapidly at ordinary temperatures, producing great cold, and boils at 46.6° C.

Exp. 175.—Place a watch-glass filled with carbonic disulphide on a glass plate covered with water, and evaporate it rapidly by blowing a current of air over its surface. The glass will be frozen to the plate.

It has never been solidified by cold. Its vapor is so inflammable that it may be ignited by a glass rod heated below redness (Fig. 87); consequently, great care should be used in experimenting with it.

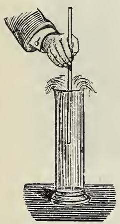

Fig. 87.

307. Chemical properties. Carbonic disulphide is a sulphur acid, capable of combining with alkaline sulphides to form sulphocarbonates, as K_2S, CS_2. It is easily decomposed into its elements, carbon and sulphur, and hence may be used to form various carbon and sulphur compounds.

308. Uses. Carbonic disulphide is an excellent solvent for phosphorus, iodine, sulphur, many resins, and oils. It is very extensively used in the extraction of fats and oils, and in the cold process of vulcanizing caoutchouc. The poisonous properties of its vapor have been turned to account for killing insects in grain.

Silicon or Silicium.

309. Silicon is always found in combination with oxygen, either alone as silicic anhydride (SiO_2), in the form of quartz or sand, or united with various metallic oxides, forming silicates.

310. Preparation. Silicon is prepared by heating dry potassium silico-fluoride with potassium or aluminium.

$$2\,KF, SiF_4 + K_4 = 6\,KF + Si.$$

311. Physical properties. Silicon may be obtained in

three forms: (1) a soft, brown, amorphous powder; (2) as hexagonal plates, which resemble graphite in luster and power of conducting electricity—sp. gr. 2.5; and (3) in iron-gray needles or octahedra, which are so hard as to scratch glass like the diamond. All these forms are fusible at a temperature between 1600° C. and 1800° C.

312. Chemical properties. Amorphous silicon burns brilliantly in air to SiO_2, and dissolves in hydrofluoric acid to SiF_4. The other forms of silicon are incombustible in air, and are insoluble in hydrofluoric acid.

Like carbon, silicon is found in cast iron and in certain other metals, either mixed or in compounds which resemble alloys; but, unlike carbon, it forms but one known compound with hydrogen, and that of a very unstable character. It must, however, be remarked that numerous alcohols and ethers are known which contain silicon in place of carbon.

313. Hydrogen silicide, H_4Si, is prepared by decomposing magnesium silicide by dilute hydrochloric acid. $Mg_2Si + 4HCl = H_4Si + 2MgCl_2$. It is a colorless gas, insoluble in water that is free from air.

314. Chemical properties. Pure hydrogen silicide is not spontaneously inflammable at ordinary temperatures, but is easily decomposed by heat into amorphous silicon and hydrogen. When mixed with hydrogen, it ignites in the air spontaneously, evolving silicic anhydride, and depositing on a cold surface a brown film of silicon.

315. Silicic anhydride, or silica, SiO_2. The purest natural variety of silica is quartz, or rock crystal. This is found in beautiful, six-sided prisms, terminated by six-sided pyramids. It also occurs crystalline very nearly pure—as amethyst, rose quartz, and Cairngorm stones; and in the amorphous form—as jasper, agate, onyx,

carnelian, chalcedony, and flint. The opal is silica combined with water. The whiter varieties of sand are nearly pure silica; the yellow color of ordinary sand and sandstones is due to the presence of an oxide of iron.

316. Preparation. The gelatinous precipitate which forms when silicon fluoride is decomposed by water, is a compound of silicic anhydride and water, which may be regarded as silicic acid. If this is washed and dried, the white powder which is left is silicic anhydride.

317. Physical properties. Quartz is so hard as to be able to scratch glass: sp. gr. 2.5 to 2.9. The artificial silica is so finely divided that it is remarkable for its extreme mobility, the slightest breath easily blowing it away. All varieties of silica are infusible except by the extreme heat of the oxy-hydrogen flame.

318. Chemical properties. Ignited silicic anhydride is insoluble in all acids except hydrofluoric. It unites with the alkalies, either on boiling with their solutions or on fusing in the dry state, forming silicates which are soluble in water. These compounds are known as soluble glass.

319. Silicic acid. If a solution of an alkaline silicate be slightly acidulated with hydrochloric acid, the gelatinous precipitate which forms is probably $2H_2O, SiO_2 = H_4SiO_4$, or orthosilicic acid. In this state it is readily soluble either in alkalies or in hydrochloric acid. Silicic acid soluble in water may also be obtained by dialysis.

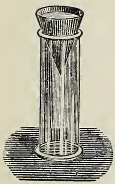

FIG. 88.

Exp. 176.—Support a cone of parchment paper in a vessel filled with distilled water, so that the water may come in contact with the outer surface of the cone, and fill the cone with a solution of silica in hydrochloric acid. In a

few days the alkaline chlorides derived from the soluble glass and the hydrochloric acid will dialyze through the paper, and a solution of silicic acid in water remain in the cone.

This solution may be evaporated *in vacuo* to a transparent glass, which is metasilicic acid, $H_2O, SiO_2 = H_2SiO_3$. The solution has a great tendency to assume the gelatinous form, and can not be preserved.

Many thermal springs also contain silica in solution. The Geysers of Iceland contain considerable quantities, and, as the liquid cools, deposit the silica upon objects exposed in their basins. In these cases we must suppose the solvent power to be due to the presence of alkaline carbonates, assisted by the high temperature. Silica dissolved in soil is taken up by plants; notably so by the cereals, grapes, and rushes. It forms beautiful crystals in the leaves of the *Deutzia scabra*.

320. The natural silicates are very numerous, and are often of a very complex nature. Among these are clay and kaolin ($Al_2O_3, 2SiO_2$), potash mica ($Al_6K_2O_{10}, 6SiO_2$), common mica ($Mg_4Al_2O_7, 2SiO_2$), garnet ($Ca_3Al_2O_6, 3SiO_2$), the feldspars, orthoclase ($K_2Al_2O_4, 6SiO_2$), and albite ($Na_2Al_2O_4, 6SiO_2$). Talc, meerschaum, serpentine, and hornblende are principally silicates of magnesia.

321. Of the artificial silicates, only those of the alkalies are soluble in water. These are largely used, under the name of soluble glass: (1) in mural paintings; (2) for the preservation of building stone; (3) for cleansing wools; and (4) in preparing mordanted calicoes for dyeing.

Glass is a mixture of an alkaline silicate with one or more insoluble silicates. Glass is made by fusing silica with potash or soda and some base which is calculated to render the mixture less soluble, more infusible, or more transparent. Crown glass is a silicate of potash and lime; flint glass is a silicate of potash and lead;

ordinary window glass is a silicate of soda and lime. The cheaper forms of glass generally contain also silicates of alumina and of iron. Ferrous oxide imparts a green color to glass, but ferric oxide gives only a yellowish tinge. Hence, the green color due to iron may be prevented by the addition of some oxidizing agent, as arsenious acid or niter. Manganese dioxide imparts a purple color to glass. If green and purple glasses are fused together, a colorless glass results. We may suppose this effect to be produced either by reason that the two colors are complementary to each other, or that the manganese acts as an oxidizing agent. Colored glass is produced by small quantities of various substances:—red, by cuprous oxide; ruby, by gold; yellow, by antimony; blue, by cobalt; white enamel, by stannic oxide. The glass used for imitation of precious stones contains generally a large proportion of lead oxide, also frequently baryta and boracic acid.

TESTS.—Silica may be recognized, (1) by its insolubility in acids; (2) by its infusibility before the blowpipe. (3) Make a bead of microcosmic salt ($NaNH_4HPO_4$) on a loop of platinum wire, and add a trace of a silicate. On again fusing the bead, the silica will remain undissolved and will float as a spongy mass (silica skeleton) in the molten bead. An excess of silica renders the bead opaque.

TIN.

322. The only important ore of tin is cassiterite, or tin stone, SnO_2. This is found mixed with other metallic ores in veins traversing the primitive rocks, and also, in a purer condition, as stream tin ore, in the alluvial deposits which are formed by the natural disintegration of these rocks. The largest supplies of tin are obtained from Cornwall, Malacca, Banca, and Australia.

323. Preparation. Tin is obtained by smelting the ore mixed with pulverized anthracite or charcoal.

324. Physical properties. Tin is a soft, white metal: sp. gr. 7.29. It fuses at 228° C., but is not easily volatilized. Its tenacity and ductility are very low, but it is highly malleable, as is shown in the manufacture of tin foil. It exhibits a considerable tendency to crystallize. A bar of tin, when bent, emits a peculiar, creaking sound, which is probably due to the interior crystals breaking against each other.

Exp. 177.—Wash the surface of tin plate with warm, dilute nitro-hydrochloric acid. In a little while, a mass of crystalline forms will appear (*moirée metallique*).

325. Chemical properties. Tin unites readily with sulphur, chlorine, phosphorus, and oxygen, when heated with these elements. It retains its luster for a long time, even in the presence of moist air; but, when fused in air, rapidly oxidizes to white stannic oxide, SnO_2. It forms two series of compounds: the stannous, in which it is bivalent, and the stannic, in which it is quadrivalent.

326. Uses. Tin is generally employed in alloys and as a coating for other metals. Tin plate is simply a sheet of iron covered with tin. It is made by carefully cleansing iron plates from every trace of oxide, and then immersing them in melted tin. A cheaper variety, terne plate, is coated with an alloy of tin and lead. Brass pins are coated with tin by boiling them in water containing granulated tin, acid potassium tartrate, alum, and common salt.

Among the alloys of tin are solder and pewter ($Sn + Pb$), Britannia metal ($Sn + Cu + Sb$), gun metal, bronze, and bell metal ($Cu + Sn$). The silvering applied to the backs of mirrors is tin foil amalgamated with mercury.

327. Stannous chloride, $SnCl_2, 2H_2O$, is obtained in prismatic needles by dissolving tin in hydrochloric acid.

It has a strong attraction both for chlorine and oxygen. and hence acts as a powerful reducing agent.

Exp. 178.—Add to a solution of $HgCl_2$ a drop or two of $SnCl_2$: calomel will be formed. $2HgCl_2 + SnCl_2 = \underset{\smile}{Hg_2Cl_2} + SnCl_4$. Now add the $SnCl_2$ in excess: the precipitate is dark gray, metallic mercury. $Hg_2Cl_2 + SnCl_2 = 2\underset{\smile}{Hg} + SnCl_4$.

Stannous chloride is converted by water into an insoluble oxychloride (Sn_2Cl_2O). This change may be prevented by the addition of either hydrochloric or tartaric acid. It is used by the dyer as a deoxidizing agent, under the name of "tin salt."

328. Stannic chloride, $SnCl_4$, may be obtained as a heavy, fuming liquid by heating tin filings in dry chlorine gas. It readily combines with a small quantity of water to form $SnCl_4, 5H_2O$; but an excess of water decomposes it. A solution of this chloride is readily prepared by dissolving tin in hydrochloric acid, to which a very little nitric acid has been added.

Stannic chloride forms double salts with the chlorides of the alkalies. The "pink salt," used by dyers in the production of red colors, is $2NH_4Cl, SnCl_4$.

329. Stannous oxide is formed as a white hydrate, $2SnO, H_2O$, by precipitating stannous chloride with sodium carbonate. On boiling this mixture, the anhydrous oxide, SnO, forms as a brown powder.

It is a weak base which dissolves in acids to form stannous salts. The moist hydrate readily absorbs oxygen and becomes stannic oxide. Caustic potash converts it into metallic tin and stannic oxide, which combines with the potash.

330. Stannic oxide, SnO_2, is formed when tin is fused in contact with the air, or when either of the hydrates are strongly ignited. It is a white powder so hard that

it is used for polishing, under the name of "putty powder." It is insoluble in acids, but, when fused with the alkalies, forms soluble compounds which are called stannates.

Sodium stannate, $Na_2O, SnO_2 = Na_2SnO_3$, is used as a mordant by calico printers. If a solution of this salt in water be acidulated with hydrochloric acid, a white, gelatinous precipitate falls; this is H_2O, SnO_2. As it readily combines with metallic oxides, it is stannic acid; but it also dissolves in the stronger acids, and forms with them stannic salts, in which it plays the role of a weak base.

Metastannic acid, $5H_2O, 5SnO_2 = Sn_5H_{10}O_{15}$, is formed by the action of nitric acid upon metallic tin. It is entirely insoluble in acids, but forms soluble metastannates with the alkalies.

331. Stannous sulphide, SnS, precipitates as a brown hydrate when hydrogen sulphide is passed into a solution of a stannous salt. When treated with the alkaline persulphides, it becomes SnS_2.

This stannic sulphide is also produced as a dull yellow hydrate when hydrogen sulphide is passed into solutions of stannic salts. It is sulphostannic acid, and dissolves easily in alkaline sulphides.

Stannic sulphide may also be produced in the dry way by carefully heating tin amalgam with sulphur and sal-ammoniac in a Florence flask. Beautiful yellow scales are left in the flask, which are called *mosaic gold*, and are used for decorative purposes.

332. Tests. The reactions mentioned in speaking of the preparation of the hydrated oxides and sulphides are tests for the salts of tin. Stannous chloride is distinguished from stannic chloride by its reducing action on mercuric chloride; and by its giving, with an excess of auric chloride, a precipitate, "the purple of Cassius" ($AuSnO_2$?). All tin compounds, when heated on charcoal with sodium carbonate, yield a malleable globule of tin.

333. Titanium and zirconium are rare tetrad elements. Titanium occurs in nature as titanic anhydride, TiO_2 (Rutile), but more frequently in iron ores as a titanate of iron. The slags obtained in smelting such ores with charcoal frequently contain copper-colored crystals which have the probable formula $Ti(CN)_2 3Ti_3N_2$. These are interesting, because they show the direct union of atmospheric nitrogen with titanium and carbon. When titanic anhydride is strongly heated in ammonia, it also forms TiN_2 (titanium nitride).

Zirconium has three allotropic states resembling those of silicium. Its principal oxide, ZrO_2 (zirconia), acts both as a base and as an acid. The sulphates of zirconium and of titanium are decomposed by a large excess of water.

Recapitulation.

These elements are grouped together because they act as tetrads, forming tetrachlorides (RCl_4) and acid anhydrides (RO_2), which form soluble salts with the fixed alkalies.

They may be divided into two sub-groups:

(*a*) Carbon, silicon.
(*b*) Titanium, zirconium, tin.

Carbon and silicon are non-metals which are remarkable for not conforming to the law of the specific heat of atoms (p. 55). Their compounds are very numerous and are of similar constitution.

The second sub-group consists of semi-metals, tin being popularly classed as a metal on account of its physical properties. Their compounds strongly resemble those of silicon.

Several of these elements form dyad compounds; as, CO, $SnCl_2$.

CHAPTER X.

THE ELECTRO-POSITIVE ELEMENTS.

334. The metals are distinguished from the elements previously studied principally in the fact that their oxygen compounds are generally basic. The semi-metals closely agree with them in their physical properties; and for this reason arsenic, antimony, bismuth, and tin will, in this chapter, be again grouped with the metals. They form undoubted alloys with the metals, and, as already stated, are a connecting link between the non-metals and the metals.

Physical Properties of Metals.

335. (I) **Great opacity.** Some metals, when in very thin sheets, are translucent. Thus, gold leaf transmits light of a green color.

336. (II) **Luster.** When the metals are very finely divided, as iron reduced by hydrogen (Exp. 30), they are generally dull looking powders; but when they are melted or beaten into a compact mass, they have in a high degree the power of reflecting light, which gives them the so-called metallic luster.

Exp. 179.—Add ferrous sulphate to gold chloride. Brown, metallic gold precipitates. On rubbing this, when dry, with a hard, smooth substance, it assumes the yellow luster of gold.

The natural luster of silver and of gold is very great. Metals which are hard enough to be polished, like iron in the form of steel, give splendid reflecting surfaces.

The mirrors or specula of the ancients were made of metals. An alloy of tin and copper is still used for this purpose in reflecting telescopes.

337. (III) **The color** of most of the metals is white or gray. Silver, tin, and sodium are almost pure white; iron, somewhat gray; lead and zinc, bluish; calcium, pale yellow; gold, full yellow; bismuth, reddish; and copper, a full red.

338. (IV) **A few metals yield a peculiar odor** when rubbed, as is the case with copper and tin. Many of their salts have an acrid *taste* which is called metallic. To the formation of these salts is due the peculiar taste observed when a tarnished piece of copper or brass is placed on the tongue.

339. (V) **Crystallization.** Many metals may be crystallized in some form of the isometric system, as the cube, octahedron, etc. The metals most easily crystallized are generally the brittle metals, as bismuth and antimony.

Exp. 180.—Melt several pounds of lead in a crucible and set it aside to cool. As soon as a crust has formed on the top, pour out the still molten interior, and a mass of interlaced octahedra will remain.

Exp. 181.—Suspend a bright strip of zinc in a dilute solution of lead acetate. After a few days, arborescent crystals of lead will be formed (*arbor Saturni*).

Some metals while in the solid state tend to assume a crystalline structure under the influence of repeated blows. The sudden breaking down of iron bridges and of iron axles in railway cars has been attributed to this cause.

340. (VI) **The cohesion of metals** varies greatly. At ordinary temperatures, mercury is a liquid; all the

others are solids. Some of these, as sodium and potassium, are so soft that they may be kneaded like wax; others, as chromium and manganese, rival the diamond in hardness.

The soft metals and the brittle metals have generally little tenacity: lead and zinc are examples. A bar of steel one square inch in section has resisted a stretching force of nearly 180,000 pounds. Copper wire has about one-third of this tenacity.

341. (VII) **Many metals are malleable**; that is, they are capable of being flattened out under the hammer or between rollers; and are also *ductile*, or capable of being drawn into fine wires. The following table, which gives the relative tenacity, ductility, and malleability, shows that the metals do not possess these properties in equal degrees.

RANK.	TENACITY.	DUCTILITY.	MALLEABILITY UNDER THE HAMMER.	MALLEABILITY BETWEEN ROLLERS.
1	Iron	Platinum	Lead	Gold
2	Copper	Silver	Tin	Silver
3	Platinum	Iron	Gold	Copper
4	Silver	Copper	Zinc	Tin
5	Zinc	Gold	Silver	Lead
6	Gold	Zinc	Copper	Zinc
7	Lead	Tin	Platinum	Platinum
8	Tin	Lead	Iron	Iron

The ductility and malleability are increased, within certain limits, by a high temperature. Iron is rolled when at a white heat; zinc is most malleable when between 105° C. and 150° C.

342. (VIII) **All the metals are fusible.** Mercury, cadmium, zinc, magnesium, potassium, sodium, and rubidium are so readily vaporized that they may be puri-

fied by distillation. Others of the metals have been volatilized, but only at high temperatures.

343. (IX) **The specific gravity** of these elements exhibits a wonderful difference. Some are lighter than water. The common metals are from seven to nine times heavier than water (lead, 11.33). The *noble metals* are the heaviest bodies known.

The following table exhibits the specific gravities and fusing points of the metals.*

ELEMENT.	SPECIFIC GRAVITY.	FUSING POINT.	ELEMENT.	SPECIFIC GRAVITY.	FUSING POINT.
Lithium	.59	180° C.	Cadmium	8.56	320°
Potassium	.86	62°.5	Molybdenum	8.63	1900°? C.
Sodium	.97	95°.6	Nickel	8.82	1800°?
Rubidium	1.52	38°.5	Copper	8.94	1200°
Calcium	1.58		Cobalt	8.51	1800°?
Magnesium	1.74	433°	Bismuth	9.8	270°
Glucinum	2.10	1000°?	Silver	10.57	1023°
Strontium	2.54		Lead	11.33	332°
Aluminium	2.56	700°?	Ruthenium	11.4	2000°?
Barium	4.	450°	Palladium	11.8	1900°?
Arsenic	5.63		Thallium	11.9	290°
Gallium	5.9	+30°	Rhodium	12.1	2000°?
Antimony	6.72	450°	Mercury	13.6	—39°.4
Chromium	7.01	1900°?	Tungsten	18.3	1900°?
Zinc	7.13	433°	Uranium	18.4	
Indium	7.42	176°	Gold	19.26	1250°
Tin	7.30	228°	Iridium	21.15	2000°?
Iron	7.84	1800°	Osmium	22.47	2000°?
Manganese	8.02	1800°?	Platinum	21.5	2000°

344. Natural history. Few of the metals are found native. Among these are bismuth, gold, and platinum, which are almost always found in the state of metals; silver, mercury, and copper, which are found native less frequently; arsenic and antimony, which are seldom found uncombined with the other elements.

* Temperatures above 1000° given in this table are only approximate.

Generally the metals occur as constituents of various minerals and ores. Lead, mercury, copper, zinc, and iron are frequently found united with sulphur. These sulphides often exhibit a brilliant luster, but have neither the ductility nor the tenacity of the metals. Tin, iron, and manganese are generally found as oxides. Calcium and sodium are sometimes met with as fluorides; and there are also chlorides of sodium and of potassium in enormous quantities.

Most of the minerals which constitute the solid crust of the globe are compounds of silica, alumina, lime, and magnesia. Thus, ordinary clay is mainly aluminium silicate; limestone is calcium carbonate; gypsum is calcium sulphate; the micas and feldspars are compounds of silica and alumina with other silicates of soda, potash, or lime; talc and serpentine are compounds of silica and magnesia. On the other hand, most of the ores which yield the metals that are useful in the arts seldom occur in large masses, but are collected in comparatively thin beds, or seams, called mineral veins.

345. Chemical properties. The metals exhibit strong affinities for the non-metals, and easily form stable compounds with them. Such, for example, are the binary compounds with oxygen, sulphur, and chlorine; as, Fe_2O_3, FeS_2, NaCl.

More commonly, ternary compounds are formed; as, for example, the hydrates of the alkalies, KHO, NaHO. The oxygen compounds, whether anhydrides or hydrates, are very generally basic. The protoxides are, almost without exception, strong bases; the strongest bases being those of the more electro-positive elements, as K, Na. The sesquioxides are generally weak bases, and in some cases may act as acids.

For example, Al_2O_3, aluminium sesquioxide, easily dissolves in sulphuric acid to form aluminic sulphate, $Al_2O_3, 3SO_3$, in which it plays the part of a base. It also dissolves easily in a solution

of potassium hydrate to form K_2O, Al_2O_3, potassium aluminate, in which it plays the part of an acid.

The higher oxides of the metals are sometimes indifferent bodies, as MnO_2, PbO_2; or, when their highest stage of oxidation is reached, acid anhydrides, such as CrO_3, MnO_3, Mn_2O_7.

346. If a metal or its oxide is dissolved in an acid, a *salt* is formed. The acid loses the whole or a part of its hydrogen, which is replaced by the metal.

The halogen compounds of the metals, as $NaCl$, $CuCl_2$, are for the most part stable salts, not decomposed by water.

The ternary salts commonly contain a metal and a non-metal, or an acid radical, united by oxygen. Practically speaking, it makes but little difference what formula is assigned to these salts, if it correctly represents the percentage composition. The tendency among chemists is to use only the molecular formulæ.

347. Almost every metal has a long series of salts, as the carbonates, sulphates, nitrates, phosphates, etc. Not unfrequently each element has, besides the normal salt, others which are either basic or acid salts.

Besides these, we have a very interesting class of double salts. These very generally contain one kind of acid, but two or more bases, as $K_2Mg, 2SO_4 + 6H_2O$, and $KAl, 2SO_4 + 12H_2O$. A complete description of all these compounds would require many volumes of this size; hence, we shall attempt to give only the most important.

348. The metals, when melted together, form alloys. Such are brass (Cu and Zn), bell metal, and bronze (Cu and Sn). These alloys seem sometimes to be true chemical compounds; but, for the most part, are to be regarded as solidified mixtures containing, perhaps, a true compound with an excess of one of the ingredients.

The alloys of mercury with the other metals are

called *amalgams.* The metallic surface of ordinary mirrors is an amalgam of mercury and tin.

349. Classification. The table on the following page, prepared by Mendelejeff, exhibits a very ingenious classification of all the elements. They are arranged in lines in accordance with their atomic weights:* the series, from left to right; the groups, from top to bottom. By this arrangement, elements which are similar in properties are brought in close juxtaposition; and thus those that show a marked gradation of properties are collected in natural groups. Some of these groups have been long recognized, as the chlorine group (7), the nitrogen group (5), the carbon group (4), which we have already studied. There are also natural groups among the metals, not less marked. Among these are the alkali group (1), the alkaline earths (2), the earths (3), which have so many points of resemblance that we might profitably consider each group as a whole before proceeding to the elements which compose it. Nevertheless, the grouping used in this book has been made rather for the convenience of the student than for the sake of any theory, however interesting and ingenious.

Recapitulation.

The metals differ from the non-metals in their physical properties; such as, opacity, luster, color, crystalline form, cohesion, tenacity, malleability, fusibility, specific gravity, etc. They also differ in their chemical properties, their lower compounds with O and S being generally basic. Some are found native, but generally as ores, containing O, S, and Cl; or as salts, containing CO_2 and SiO_2.

The compounds of the metals with each other are called alloys or amalgams.

All the elements may be so grouped as to show a natural gradation of properties.

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* Mendelejeff's atomic weights are frequently different from those on pp. 12 and 13, 59, and 60.

THE ELEMENTS.

SERIES.	Group 1.		Group 2.		Group 3.		Group 4.		Group 5.		Group 6.		Group 7.		Group 8.			
	$RCl-R_2O$		RCl_2-RO		$RCl_3-R_2O_3$		RCl_4-RO_2 H_4R		$RCl_5-R_2O_5$ H_3R		RCl_6-RO_3 H_2R		$RCl_7-R_2O_7$ HR		RO_4, R_2O_3, RO, R_2O			
I	H 1																	
II		Li 7		G 9.4		B 11		C 12		N 14		O 16		F 19				(Na 23)
III	Na 23		Mg 24		Al 27.4		Si 28		P 31		S 32		Cl 35.5					
IV		K 39.1		Ca 40		Sc 44		Ti 50		V 51.2		Cr 52.2		Mn 55	Fe 56	Co 59	Ni 58	Cu 63
V	(Cu 63)		Zn 65.1		Ga 69.9		—72		As 75		Se 79		Br 80					
VI		Rb 85		Sr 87.6		?Yt 88		Zr 89.6		Nb 94		Mo 96		—100	Ru 104	Rh 104	Pd 105	Ag 108
VII	(Ag 108)		Cd 112		In 113.5		Sn 118		Sb 122		Te 125?		I 127					
VIII		Cs 133		Ba 137		La 138		?Ce 140		Di 146		Tb 149						
IX					Tr 148				Er 166									
X						Yb 173				Ta 182		W 184			Os 198?	Ir 193	Pt 194	Au 196
XI	(Au 196)		Hg 200,		Tl 204		Pb 207		Bi 210		Ng 214							
XII								Th 231				U 240						

CHAPTER XI.

THE ALKALI METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C.	DISCOVERER.
Lithium	Li	7	0.578	180°	Arfwedson, 1817.
Sodium	Na	23	0.97	95°.6	Davy, 1807.
Potassium	K	39.1	0.865	62°.5	Davy, 1807.
Rubidium	Rb	85.4	1.52	38°.5	Bunsen, 1860.
Caesium	Cs	133	1.88	26°.5	Bunsen, 1860.
Ammonium	NH_4	18			
Silver	Ag	108	10.57	1023°	

350. The metals of this group are all monads, forming but one chloride, RCl. The first five—lithium, sodium, potassium, rubidium, and caesium—are the alkali metals. The salts of the hypothetical ammonium are very like those of potassium, and hence it is convenient to study them at this place. Silver is not an alkali metal, but may be reckoned as a sub-group. Some of its salts are isomorphous with those of sodium.

351. The alkali metals have the following properties in common: (1) They may be obtained by the electrolysis of their fused chlorides.

(2) They are soft, light, easily fusible metals which volatilize at high temperatures.

(3) When freshly cut, they possess a strong metallic luster; but, when exposed to the air, they soon tarnish and form white oxides of the formula R_2O. Their affinity for oxygen increases with their atomic weight. When caesium is set free by electrolysis, it takes fire as soon as it is exposed to the air; and hence it has not as yet been obtained except as an amalgam.

(4) Owing to their strong affinity for oxygen, these metals decompose water at all temperatures, setting free its hydrogen. The oxides thus formed dissolve in the excess of water to form hydrates of the formula R_2O, H_2O or RHO. These hydrates can not be deprived of their water by heat alone.

(5) The alkaline hydrates are the strongest bases known, completely neutralizing every acid. They change infusions of red cabbage or violets to green; turmeric, to brown; and restore litmus, which has been reddened by acids, to blue. In a concentrated form they destroy animal and vegetable tissue, acting "caustic." Their taste is acrid and unpleasant.

(6) When these hydrates are exposed to the air they form white carbonates. These alkaline carbonates can not be decomposed by heat alone. They are all soluble in water (lithium somewhat sparingly), and their solutions react alkaline to test papers.

(7) All these elements are very widely diffused, although none of them are found native. Their chlorides are found in very many mineral springs, and are frequently associated together. They are also found in the ashes of many plants, and not unfrequently in minerals. Nevertheless, only sodium and potassium are found in large quantities.

Sodium.

352. Sodium, Na, is the most abundant of the alkali metals. It is distributed very widely. As a chloride

(NaCl), it is found in the sea water, in salt springs, and in both vegetables and animals. It is also found in many minerals, as rock salt, Chili saltpeter ($NaNO_3$), and some silicates.

353. The metal was first prepared by Davy, in 1807, by electrolysis. It is now prepared on a large scale by heating an intimate mixture of dry sodium carbonate with charcoal to a white heat: $Na_2CO_3 + 2C = Na_2 + 3CO$. At this temperature the carbon reduces the sodium, which distills over and is collected under petroleum. It is then purified by remelting under a thin layer of petroleum, and is cast into bars.

354. Physical properties. Sodium is a silver-white metal, with a brilliant luster when freshly cut, soft like wax, and easily moulded by the hand. Its specific gravity is a trifle less than that of water. It oxidizes rapidly even in dry air, and must be kept under petroleum. When thrown upon water, it decomposes it readily; but the heat evolved is not generally sufficient to enkindle the hydrogen set free.

Exp. 182.—Place a bit of filter paper on the surface of the water, and upon it a pellet of sodium. The sodium will be prevented from rotation, and will oxidize so rapidly as to ignite the hydrogen. The yellow color of the flame is due to the sodium vapor which is simultaneously burned. The water contains sodium hydrate, and reacts alkaline to turmeric paper and to reddened litmus.

355. Sodium is a powerful reducing agent, and is largely used in the preparation of aluminium and magnesium. Its amalgam has recently been employed in the reduction of silver ores.

Exp. 183.—Shake together in a test tube a piece of sodium with an equal bulk of mercury. The two metals will combine with a sharp flame, and, on cooling, form a solid mass (sodium amalgam). This may be employed in reducing silver chloride, or reserved for experiments. (See **Exp. 189**).

356. The salts of sodium are, perhaps, the most important known to chemists. Almost every acid forms a sodium salt, easily soluble in water, and crystallizing from concentrated solutions in well-defined forms. Some of these have received a wide application in the arts, and therefore require a more extended notice than we shall be able to give to those of the metals following.

357. Sodium chloride, $NaCl$, is our *common salt* used in cooking. It is found in Europe in enormous quantities as rock salt. In the United States it is generally obtained by evaporating the waters of salt springs. Millions of tons are manufactured annually from the salt springs of New York, Michigan, Ohio, and West Virginia.

Sodium chloride is about equally soluble in cold and hot water. A saturated brine contains about 26 per cent of salt. From such saturated solutions the salt crystallizes out in beautiful cubes, which sometimes are so attached by their edges as to form hopper-shaped masses. This peculiarity is common to all of the halogen compounds of the alkalies.

The uses of salt as a condiment and in preserving meats are well known. It also finds some employment as a cheap glazing for pottery, and is the source from which most of the other salts of sodium are obtained.

358. Sodium sulphate, Glauber's salt, $Na_2SO_4 + 10H_2O$, occurs frequently in mineral springs, and is used in medicine. It is manufactured in enormous quantities by heating sodium chloride with sulphuric acid. In this process immense quantities of hydrochloric acid are evolved, which are absorbed by passing the gas through towers filled with coke over which a stream of water is constantly trickling. The operation has two stages: (1) The acid first forms an acid sodic sulphate, at a comparatively low temperature; thus, $NaCl + H_2SO_4 =$

$NaHSO_4 + \widehat{HCl}$. (2) The temperature is then raised, when the acid sodic sulphate acts upon the remaining portion of the salt to form the normal sulphate, $NaCl + NaHSO_4 = Na_2SO_4 + \widehat{HCl}$. The product thus formed is called *salt-cake.* If dissolved in water and crystallized out at ordinary temperatures, it retains ten molecules of water and forms monoclinic prisms which effloresce in dry air.

Exp. 184.—When a solution of this salt, saturated at 33° C., is left undisturbed to cool, it forms a so-called supersaturated solution which may be kept for days without crystallizing. If, after cooling, a crystal of the salt be dropped into the solution, the whole solidifies to a mass of the ordinary crystals, with a marked increase of temperature.

359. Sodium carbonate, Na_2CO_3, is made by roasting salt-cake with about an equal weight of chalk and a little more than half its weight of coal.

The chemical change consists mainly, (1) in the action of the carbon upon the sodium sulphate, whereby sodium sulphide is formed: $Na_2SO_4 + 4C = Na_2S + 4\widehat{CO}$. (2) In the action of the carbon upon the chalk, whereby the calcium carbonate becomes calcium oxide: $CaCO_3 + C = CaO + 2\widehat{CO}$. (3) When this resulting mass of sodium sulphide, calcium oxide, and unaltered calcium carbonate is treated with water, there forms an insoluble oxy-sulphide of lime, and sodium carbonate is dissolved out: $2Na_2S + CaO + 2CaCO_3 = 2Na_2CO_3 + CaO, 2CaS$. (4) The solution thus obtained is allowed to stand, and forms crystals of the formula $Na_2CO_3 + 10H_2O$. These crystals easily effloresce, losing their water of crystallization and becoming anhydrous Na_2CO_3.

360. The "bicarbonate" of soda, $Na_2O, H_2O, 2CO_2$ or $NaHCO_3$, or acid sodium carbonate, is easily formed by passing into a solution of sodium carbonate a stream of carbonic anhydride.

Sodium carbonate is largely used in the manufacture of glass and of soap, and is the usual *sal-soda* of commerce. Sodium bicarbonate is used in medicine, and is one of the constituents of most baking powders.

361. Sodium hydrate, NaHO, is formed by heating sodium carbonate with an excess of slaked quicklime.

$$Na_2CO_3 + Ca(HO)_2 = 2NaHO + CaCO_3.$$

A considerable quantity is always formed in the process given in § **359,** because of the excess of the chalk and coal used. When its solution is evaporated to dryness, it forms a white, solid, fusible mass, soluble in water, with considerable evolution of heat. It is a very strong base, acting very caustic upon the skin, and readily combining with oils to form hard soaps.

362. Sodium nitrate, $NaNO_3$, is found in large quantities in Peru. It is used in the manufacture of blasting powder; but as it readily deliquesces in moist air, it can not be employed for the manufacture of ordinary gunpowder. It finds an extensive use in the manufacture of ordinary saltpeter, nitric acid, and fertilizers.

363. Di-sodium phosphate, $Na_2HPO_4 + 12H_2O$, is obtained by adding sodium carbonate to phosphoric acid or to its lime salt. It crystallizes in rhombic prisms, which effloresce in dry air. The salt dissolves in four parts of cold water, and yields a solution feebly alkaline. There are several other sodium phosphates.

364. The sodium silicates are also very numerous, and, at the same time, a very interesting set of compounds. When caustic soda and quartz sand are fused together, a silicate of soda is formed. The formula of the resulting compound will vary with the proportions used, as silicic acid possesses in a wonderful degree the property of forming the so-called "condensed" salts. The "water glass" of commerce has very nearly the formula $2Na_2O, 5SiO_2$. It is soluble in water, and is used for the preparation of artificial stone, for the manufacture of fire-proof paints, and is also used in some kinds of soap.

Potassium.

365. Potassium resembles sodium in most of its properties, and is frequently found associated with it in nature. It exists in sea water; in many mineral springs as KCl. Large deposits of the solid chloride have recently been discovered at Stassfurth. It is also a constituent of the common feldspars and micas. These minerals, decomposing through atmospheric influences, become important agents in soils, and yield their potash to growing plants. From these it is again transferred to animals, and becomes an important constituent of milk, blood, and flesh.

The principal source from which the potassium compounds are obtained is the ashes of plants. When a plant is burned, the organic salts of potash are decomposed and the carbonate is formed. This is exhausted by water, and forms *potash lye.*

366. The manufacture of the metal is effected by heating its acid tartrate in closed iron retorts.

(1) At a low heat, the tartrate is converted into an exceedingly intimate mixture of potassium carbonate and charcoal. (2) This mixture is then raised to a white heat; the metal is reduced and distills over: $K_2CO_3 + 2C = 2K + 3\widehat{CO}$. (3) The product is received under petroleum. It is contaminated with a black, explosive compound of potassium and carbonic oxide, and requires to be again distilled in order to obtain the metal in a pure state.

367. Potassium is a soft metal, having a bluish tinge and a brilliant luster. At 0° C., it is brittle; at ordinary temperatures it may be moulded like wax, and two fresh surfaces easily welded together. It melts at 62.5° C., and at a red heat volatilizes with a beautiful green vapor.

It is one of the lightest of metals: sp. gr. 0.86.

It is strongly electro-positive, and exhibits a remarkable affinity for oxygen. When exposed to dry air, its

surface becomes almost immediately covered with the protoxide K_2O. It decomposes water at all temperatures, and with sufficient energy to ignite both itself and the hydrogen set free. The flame produced is a rich violet, and is characteristic.

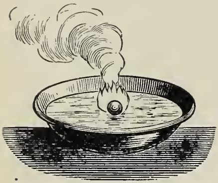


FIG. 88.

Owing to the expense of manufacturing potassium, it is not employed in the arts, being replaced by its congener sodium.

Exp. 185.—Make a small cavity in a lump of ice, and drop in this a small pellet of potassium. It will take fire and burn. Test the liquid remaining after the potassium has disappeared. It contains potassium hydrate and reacts alkaline.

$$H_2O + K = KHO + \hat{H}.$$

Exp. 186.—The strong affinities of potassium may be further shown by (1) placing a dried pellet in a deflagrating spoon, (2) melting the metal, and then (3) plunging it into various gases; as, CO_2, Cl, H_2S. It decomposes carbonic anhydride, setting free its carbon, and combines with chlorine with evolution of light.

368. Compounds of potassium. When the ashes of plants are lixiviated with water, a dark-colored lye is obtained which contains all the soluble salts of the ash. This lye, boiled down to dryness, constitutes the crude "potash" of commerce. It consists mainly of potassium carbonate; it also generally contains some potassium sulphate and some sodium salts.* If the dark color of crude potash is destroyed by roasting, it forms "pearl ash." Pure potassium carbonate is best obtained by igniting the acid tartrate or oxalate.

369. Potassium carbonate, K_2CO_3, is a white, deliquescent salt, very readily soluble in water. It has a strong alkaline taste and reaction.

* In some American potashes there exists a very considerable amount of sodium carbonate.

It was formerly of greater importance in the arts than now; but is still very largely used in the preparation of soft soap, of some kinds of glass, and in the preparation of other salts of potassium.

370. The acid potassium carbonate, $KHCO_3$, is formed by passing carbonic anhydride through a solution of the preceding in four parts of water. Beautiful monoclinic prisms soon separate out. It was formerly much used, under the name of saleratus, in baking powders and in effervescing drinks.

When the acid carbonate is heated, it loses water and half of its carbonic acid, and returns to the state of a normal carbonate. No amount of heat will expel the carbonic acid remaining. If, however, its not too concentrated solution is treated with quicklime, it is decomposed and yields

$$K_2CO_3 + Ca(HO)_2 = CaCO_3 + 2KHO.$$

371. Potassium hydrate, KHO. The solution thus formed is poured off and evaporated to dryness in iron or silver vessels. The solid hydrate is a hard, brittle, white, deliquescent mass, fusible below red heat. It readily absorbs carbonic anhydride from the air; but as it is soluble in alcohol, while the carbonate is not, an alcoholic solution of a partially altered mass will contain only the hydrate.

It is one of the strongest bases known, completely neutralizing the strongest acids, and displacing most other bases from their salts. Its taste is nauseous, and its solution, when concentrated, is highly corrosive to organic tissues. It is employed in medicine as a caustic, whence it is called *caustic potash.* It combines with fats to form soft soaps.

Exp. 187.—Add a solution of potassium hydrate to any salt of iron or copper. The iron or copper oxide will precipitate, and the potash remain in solution, combined with the acid of the salt.

372. Potassium chloride and potassium chlorate are formed when a solution of potassium hydrate is treated with chlorine. The reaction has already been described (Art. **136**). The Stassfurth carnallite ($MgCl_2$, $KCl + 6H_2O$) promises to be an abundant source for the manufacture of potassium carbonate. The process is similar to that described for the preparation of sodium carbonate.

Similarly, potassium bromide and potassium iodide are formed when bromine and iodine are added to solutions of potassium hydrate until the solution becomes very slightly colored: $6Br + 6KHO = 5KBr + KBrO_3 + 3H_2O$. Small quantities of bromates or iodates are formed at the same time. These may be separated out by crystallization, or decomposed by heating into oxygen and the halogen salts.

All these salts (KCl, KBr, KI) crystallize in cubes like common salt, and have a pleasant saline taste. The two latter are largely employed in medicine and in photography.

373. There are five potassium sulphides. We shall describe two only. If sulphuretted hydrogen gas is passed into potash lye to full saturation, the sulphydrate is formed: $KHO + H_2S = KHS + H_2O$. If this solution is mixed with an equal quantity of the potash lye, the monosulphide is formed: $KHS + KHO = K_2S + H_2O$. Both of these salts, when treated with acids, evolve sulphuretted hydrogen, and are used to form sulphides of many of the metals in the wet way. They are strong sulphur bases, and easily combine with the sulphides of arsenic, antimony, and tin to form soluble sulphur salts.

374. Potassium nitrate, KNO_3, saltpeter, occurs naturally in the soils of many hot countries, and as an efflorescence in some caverns. It is formed artificially

by the oxidation of nitrogenous organic bodies in the presence of strong bases like lime. Large heaps of organic matters, mixed with old mortar and lime, are freely exposed to the air, but protected from rain by a roof. These heaps are moistened from time to time with stable drainings, and finally lixiviated. The resulting calcium nitrate, when treated with potassium carbonate, yields potassium nitrate. It is now abundantly prepared by boiling together solutions of Chili saltpeter and potassium chloride: $NaNO_3 + KCl = KNO_3 + NaCl$. The sodium chloride first crystallizes out, and then the saltpeter, in long six-sided prisms.

The principal use of saltpeter is in the manufacture of fireworks and gunpowder.

Its taste is saline and cooling. When heated, it melts at 340° C., and then decomposes into oxygen and potassium nitrite. From the ease with which it gives up its oxygen, it is a powerful oxidizing agent.

Exp. 188.—Ignite a piece of charcoal and throw upon it a little saltpeter: it will deflagrate brilliantly.

375. Gunpowder is an intimate mixture of about 75 parts of saltpeter, 13 parts of sulphur, and 12 parts of charcoal. This amounts very nearly to $2KNO_3 + S + 3C$. It must, however, be remembered that it is not a compound, but a mixture. The materials are (1) pulverized, thrown together, moistened, and thoroughly mixed by grinding under an edge mill. (2) It is then subjected to great pressure, whereby it forms a compact mass. (3) This is broken in pieces of different sizes, which are sorted by sieves. (4) The powder is then dried by steam heat, and is frequently glazed with plumbago.

When gunpowder is fired, its explosive force is due to gaseous products such as CO_2, CO, N, and O; but besides these there are many solid products, as K_2SO_4, K_2CO_3, K_2S, etc.

Saltpeter has also some power as an antiseptic, and is used in the manufacture of nitric acid.

376. Potassium sulphate, K_2SO_4, is a by-product in the manufacture of nitric acid. When an excess of sulphuric acid is used, the acid potassium sulphate $KHSO_4$ forms. The latter, heated to about 200° C., gives off water and forms the so-called anhydrosulphate $K_2S_2O_7$ or SO_3, K_2, SO_4. At a still greater heat, sulphuric anhydride is evolved, leaving the normal sulphate K_2SO_4.

377. Caesium and rubidium are very widely distributed in mineral waters and the ashes of many plants, but, nevertheless, in exceedingly small quantities. More strongly electro-positive than potassium, they resemble it in most particulars, but are distinguished from it by the greater insolubility of their salts, and the colors which their salts yield in the spectrum. (See Art. 417).

Ammonium.

378. When a solution of ammonia in water is neutralized by an acid, a salt is formed which is very similar to the corresponding salt of potassium. It is convenient to consider that these salts contain a monatomic radical *ammonium*, NH_4, which acts like an atom of potassium, although this radical has never been isolated. (See Art. **204**).

Exp. 189.—Add to a strong solution of ammonium chloride a pellet of sodium amalgam. (Exp. 183). A bulky mass of the consistence of butter forms, which was once thought to be ammonium amalgam, NH_4Hg'. However, it differs in many respects from sodium amalgam, and soon decomposes into mercury, free ammonia, and hydrogen.

379. The solution of ammonia in water may be regarded as NH_4HO, ammonium hydrate, or aqua ammonia. It corresponds in most of its chemical reactions

to potassium hydrate, but has never been obtained in the solid state. It smells strongly of ammonia, and readily gives off this gas upon boiling.

380. **When nitrogenous bodies** decay, or when horns, bones, etc., are subjected to destructive distillation, an impure ammonium carbonate is formed. The same product is found in the ammoniacal liquors obtained in the manufacture of illuminating gas from coal. These liquors are now the chief source of ammonium salts. When treated with quicklime, they yield gaseous ammonia; with sulphuric acid, ammonium sulphate; with hydrochloric acid, ammonium chloride.

381. **The ammonium chloride,** NH_4Cl, thus formed is purified by first evaporating the liquid to dryness, and then heating the dried product. The ammonium chloride sublimes without previous melting, and collects in tough, fibrous masses in the receiver. It dissolves in its own weight of water at 100° C., and, on cooling, crystallizes out in white, feathery aggregations of cubes or octahedra.

It is an interesting fact that the vapor of ammonium chloride has but half the density due to theory (1.86). To account for this, it is supposed that the vapor (two molecules) is decomposed into two volumes of NH_3 and two of HCl, no longer combined, and therefore not condensed. This phenomenon is called *dissociation.* On cooling, the two gases again combine.

Ammonium chloride is extensively used in medicine. It dissolves many oxides, as zinc, and hence is used in soldering. It is also the principal source from which most of the other salts of ammonia are formed.

382. **Ammonium carbonate** is made by heating a mixture of ammonium chloride and calcium carbonate. The carbonate thus formed is a white, easily soluble mass,

strongly smelling of ammonia, having the probable formula of $2NH_4O, 3CO_2 + 3H_2O$. It is the *sal-volatile* of the apothecary.

There are two other carbonates of ammonia. The acid carbonate, NH_4, H, CO_3, forms when the preceding sesquicarbonate is exposed to the air as a white, almost odorless powder, somewhat difficultly soluble in water. The normal carbonate, $(NH_4)_2CO_3$, has never been obtained except in solution.

383. Ammonium sulphate, $(NH_4)_2SO_4$, is important only because it is sometimes used in the manufacture of other ammonium compounds, especially of ammonia alum.

384. Ammonium nitrate, NH_4NO_3, is a deliquescent salt, very easily soluble in water. When the dry salt is heated gradually to about 240° C., it decomposes into nitrous oxide and water: $NH_4NO_3 = N_2O + 2H_2O$.

385. Microcosmic salt, $Na, NH_4, H, PO_4 + 4H_2O$, is of great importance in blowpipe operations. When heated, it first loses its water, then its ammonia, and becomes a glassy, transparent mass of sodium metaphosphate, which has the property of dissolving many metallic oxides with characteristic colors.

386. Ammonium sulphide, $(NH_4)_2S$, is prepared by saturating aqua ammonia with sulphuretted hydrogen, and then adding an equal quantity of aqua ammonia.

$$(1)\ (NH_4)HO + H_2S = NH_4HS + H_2O.$$
$$(2)\ NH_4HS + NH_4HO = (NH_4)_2S + H_2O.$$

When first prepared it is very nearly colorless, but gradually becomes yellow, or even red, by reason of the formation of higher sulphides. By long standing it is fully decomposed, with separation of white sulphur. It is a very important agent in analytical chemistry.

Exp. 190.—Add $(NH_4)_2S$ to a solution of a zinc salt. White ZnS separates out.

Exp. 191.—Add $(NH_4)_2S$ cautiously to a solution of tartar emetic. At first, an orange sulphide of antimony precipitates; but, on adding more $(NH_4)_2S$, it redissolves to form the sulphantimonite $(NH_4)_2S, Sb_2S_3$.

387. Ammonium bromide, NH_4Br, and ammonium iodide, NH_4I, are colorless, crystallizable salts, which are extensively used in photography and have some employment in medicine.

Lithium.

388. Lithium is the lightest of the metals, floating even upon naphtha. It occurs in many minerals and mineral springs; notably in a spring in Cornwall, England, which yields daily 800 pounds of lithium chloride.

In its general properties it resembles sodium, but the sparing solubility of its carbonate and phosphate ally it to magnesium. It may, therefore, be regarded as a connecting link between the alkalies and the alkaline earths.

Its citrate and carbonate are used in the treatment of rheumatism.

Tests for the Alkalies.

(1) All alkaline salts, when boiled with milk of lime, yield solutions of alkaline hydrates. These solutions turn turmeric paper brown, and restore the color of reddened litmus. Ammonia alone yields a volatile product, which may be recognized by its peculiar odor, and by its yielding white fumes in the presence of strong hydrochloric acid.

(2) In solutions not too concentrated, lithium alone yields a precipitate with sodium di-phosphate and sodium carbonate.

(3) In moderately strong solutions, an excess of tartaric acid yields, with salts of NH_4, K, Cs, and Rb, white crystalline precipitates of acid tartrates, somewhat freely soluble in boiling water.

(4) In solutions acidified with HCl, platinum tetrachloride, $PtCl_4$, yields yellow crystalline precipitates of the formula $2RCl, PtCl_4$, with salts of NH_4, K, Cs, Rb.

(5) K, Cs, Rb, Li, and Na, when heated in a non-luminous flame, tinge the flame with characteristic colors, which have fixed places in the spectrum. (See Spectrum Analysis).

SILVER.

389. This beautiful metal not unfrequently occurs native. Its most abundant ore is the sulphide; but this is generally associated with other sulphides, as those of arsenic, antimony, and lead. It occurs less frequently in combination with Cl, Br, and I.

390. The method of extracting silver from its ores depends upon the character of the minerals with which it is associated. The so-called *amalgamation* process is, perhaps, the most common. The sulphides are (1) roasted with common salt, whereby all the silver is converted into silver chloride. (2) The resulting mass is then mixed with iron scraps and water, and placed in huge wooden casks which are made to revolve by machinery. The silver is reduced to the metallic state, $2AgCl + Fe = FeCl_2 + 2Ag$. (3) Mercury is then added in sufficient quantity to form a fluid silver amalgam, which is then drawn off from the earthy matters remaining, and washed. (4) The excess of mercury is pressed out, and the remaining amalgam heated in iron retorts. The mercury distills over, and metallic silver (often containing gold) remains behind.

391. The silver produced in Europe is obtained principally from galena, PbS, which very generally contains silver. By Pattison's process, lead ores containing not more than three ounces to the ton can be profitably worked. (1) On smelting the ores, all the silver is obtained as an alloy with the lead. (2) This alloy is melted in large iron kettles and allowed to cool gradually. Crystals of lead form, which are removed by iron strainers. (3) This process is repeated with the residue until a rich alloy of silver is obtained. (4) The final process is by *cupellation*, which consists in oxidizing the lead in a shallow vessel made of bone ash, by a

flame which is made to play over its surface. The lead oxide (litharge) is partly driven away and partly sinks into the cupel, while pure silver remains behind.

392. Pure silver does not oxidize in the air; but, when in the melted state, has the curious property of absorbing 22 volumes of oxygen. When the metal cools, the oxygen escapes and bursts through the solidified crust, giving rise to the phenomenon called the "spitting of silver." Pure silver is quite soft, and is never used in the arts. Silver plate and coins contain ten per cent of copper.

Pure silver may be prepared from coin by (1) dissolving in nitric acid; (2) precipitating the silver, as AgCl, by hydrochloric acid; and (3) reducing the thoroughly washed silver chloride by zinc. Thus prepared, it is a brown powder which may be melted at 1000° C. into a solid mass.

Silver is the whitest of the metals, very malleable and ductile, and the best conductor of heat and of electricity. It readily blackens in air containing sulphuretted hydrogen, owing to the formation of silver sulphide. It is scarcely acted upon by hydrochloric acid; but, when heated with strong sulphuric acid, dissolves, forming a silver sulphate sparingly soluble in water: $2Ag + 2H_2SO_4 = 2H_2O + SO_2 + Ag_2SO_4$. Its best solvent is nitric acid, with which it forms

$$4Ag + 6HNO_3 = 3H_2O + N_2O_3 + 4AgNO_3.$$

393. Silver nitrate, $AgNO_3$. This salt crystallizes in anhydrous, rhombic plates. These melt at 219° C., and form, on cooling, a hard mass which is used by surgeons under the name of *lunar caustic*. When moistened and applied to the flesh, it quickly and completely destroys the vitality of the part. When pure, it is not altered by sunlight; but, when in contact with organic matters, soon blackens and is reduced to the metallic state.

Hence, it stains the skin black; and hence, also, its use as an ingredient of indelible ink and of many hair dyes. It is the only salt of silver freely soluble in water, and is used to prepare most of the other silver salts. Sodium hydrate added to its solution precipitates

394. Silver oxide, Ag_2O, a brown, amorphous powder, which is a strong base, but is decomposed by heat into oxygen and metallic silver.

395. Silver chloride, $AgCl$, is readily formed from a solution of silver nitrate, by adding to it HCl or any soluble chloride. It forms a white, curdy precipitate, insoluble in nitric acid, but soluble in ammonia and in sodium hyposulphite. On exposure to sunlight, it rapidly blackens, losing chlorine and forming, as is probable, a sub-chloride of silver, Ag_2Cl. Whatever be the change, the blackened chloride is no longer soluble in sodium hyposulphite. The art of producing photographs upon paper is largely dependent upon this molecular change.

396. Silver bromide, $AgBr$, is prepared by adding to the solution of the nitrate any soluble bromide, as KBr. It has a yellowish tinge, and is somewhat sparingly soluble in ammonia, and less sensitive to light than the chloride.

397. Silver iodide, AgI, precipitates as a yellow powder almost insoluble in ammonia, when a soluble iodide, as KI, is added to a solution of silver nitrate. On exposure to light, it is scarcely altered in color, loses no iodine, but suffers an unexplained molecular change.

398. Photography, as now practiced, consists essentially of two processes: (I) the preparation of a negative picture on glass; (II) the printing of positive pictures from this upon paper.

I. (1) A clean plate of glass is thinly coated with a solution of collodion containing various bromides and

iodides, as CdI, NH_4I, NH_4Br. This rapidly dries, and forms a thin but coherent film upon the glass. (2) The plate is then dipped in a solution of silver nitrate, whereby a sensitive film of silver iodide and bromide is formed. (3) It is then exposed in a camera for a few seconds. The film does not suffer any visible alteration, but some molecular change takes place, in consequence of which a latent image is formed. (4) This latent image is *developed* by pouring upon the film a solution of ferrous sulphate. The ferrous sulphate reduces the silver, which has been acted upon by the light, and forms a *negative* picture; that is, one in which the lights and shades of an ordinary drawing are reversed. (5) The plate is then protected from the further action of light by washing in a solution of sodium hyposulphite, to remove the unchanged silver salts, and then in a large quantity of water. (6) The film is finally coated with a thin film of varnish to protect it from injury.

II. To obtain a positive picture upon paper, or one in which the lights and shadows are in their natural positions, (1) a sheet of white paper is coated upon one side with a layer of albumin containing ammonium or sodium chloride. (2) This paper is rendered sensitive by washing with a solution of silver nitrate, which is thereby converted to silver chloride. (3) The paper thus prepared is placed, when dry, behind a negative picture and exposed to the sunlight. (4) The exposed portions of the chloride are reduced and blacken, forming a positive picture. (5) It remains now only to dissolve out the unaltered chloride by sodium hyposulphite and water, in order to render the picture permanent; but, (6) as the silver thus reduced has an unpleasant red color, the picture is "toned," to give it a more agreeable tint. This is effected by steeping the paper in a solution containing a little gold chloride until the desired tint is obtained. (7) Finally, it is again washed, dried, and mounted.

399. Positive pictures may also be obtained upon glass, by a short exposure in the camera, and not too strong development. They are then placed upon a dark background. The reduced silver conceals the black ground and reflects the lights, while the transparent portions allow the black ground to show through, and thus represent the shadows of the picture.

Tests.—Most silver salts are insoluble in water, and hence a solution of silver nitrate yields precipitates with phosphates, arsenites (yellow); arseniates, chromates (red); oxalates, chlorides, bromides, iodides (white or yellowish); and sulphides (black). All of these except the last two (AgI and Ag_2S) are soluble in ammonia.

A sufficient test for silver in its solutions is obtained by adding HCl to them. The white, curdy $AgCl$ is characteristic.

Insoluble silver compounds, mixed with dry sodium carbonate and heated upon charcoal, yield a globule of metallic silver, which may be dissolved in nitric acid and tested in the wet way — by $K_2Cr_2O_7$, HCl, and NH_4HS.

Recapitulation.

Review § 351.

The alkali metals closely resemble each other in their physical properties.

As a general rule, their specific gravities, electro-positive characters, and the basicity of their hydrates increase with their atomic weights: their melting points decrease.

Their salts are generally soluble in water.

In most chemical reactions, the compounds of any one of them (and of ammonium) may take the place of any corresponding compound of any other: allowance must, however, be made for difference in solubility.

Silver differs essentially from the alkalies in its high specific gravity and melting point, as well as in its weak affinity for oxygen, and the difficult solubility of most of its salts in water.

CHAPTER XII.

THE DYAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C.	VOLATILIZES. °C.	DISCOVERER.
Calcium	Ca	40	1.58			Davy, 1808.
Strontium	Sr	87.5	2.5			Davy, 1808.
Barium	Ba	137	4.	450°		Davy, 1808.
Lead	Pb	207	11.4	325°		
Magnesium	Mg	24	1.74	433°		Bussy, 1829.
Zinc	Zn	65	7.1	412°	1040°	
Cadmium	Cd	112	8.7	320°	860°	Stromeyer, 1818.
Mercury	Hg	200	13.6	—39°.4	350°	
Copper	Cu	63.4	8.9	1200°.		

400. Calcium, strontium, and barium constitute the group of the *alkaline earths*, and are characterized by strongly marked gradational properties.

The metals have been obtained only in small quantities by the electrolysis of their fused chlorides, as moderately hard, yellowish solids, fusible below red heat. The chlorides have the general formula RCl_2, and hence these elements are dyad. $CaCl_2$ and $SrCl_2$ are deliquescent and are soluble in alcohol; $BaCl_2$ is not deliquescent, and is not soluble in alcohol.

Their compounds resemble those of the alkalies, and frequently replace them in commercial operations. Barium has the greatest chemical activity, and possesses alkaline properties in a more marked degree than the others. Its hydroxide $Ba(OH)_2$ can not be decomposed by heat alone, and is easily soluble in water. The nitrates and carbonates of this group may be decomposed by heat, yielding anhydrous oxides of the formula RO, which readily slake, and unite with water forming hydroxides, like $Ca(OH)_2$. Their solutions show a decidedly alkaline reaction. These hydroxides saponify the fats, but the resulting soaps are insoluble in water. These elements also form peroxides RO_2, which, when decomposed by dilute hydrochloric acid, yield peroxides of hydrogen, H_2O_2. Their carbonates, phosphates, and sulphates are nearly insoluble in water. Their most abundant sources are their carbonates and sulphates, which are often found associated together.

401. Lead is added to this group because many of its salts are similar to those of barium. Its carbonate, phosphate, and sulphate are insoluble in water. It acts as a dyad metal in most of its compounds, as $PbCl_2$, PbO; but sometimes acts as a tetrad, especially in some organic compounds, as $Pb, (C_2H_5)_4$, plumbic ethide.

Calcium.

402. The compounds of calcium are very widely and abundantly distributed. They occur in enormous quantities as carbonates, in marble, chalk, and limestone; as sulphates, in gypsum and alabaster; as silicates, in many minerals, *e.g.* labradorite; and less frequently as fluorides, in fluor spar. It is also an almost invariable constituent of vegetables and animals, being especially concentrated in shells, corals, teeth, and bones.

403. Calcium carbonate, $CaCO_3$, has a great variety of crystalline forms which are referable to two systems: (1) the hexagonal, represented by Iceland spar; (2) the trimetric, represented by aragonite. It is found in the ashes of plants, in egg-shells, in bones, corals, and in the shells of mollusks. The enormous masses of limestone, which serve as building stones, are largely made up of the broken and pulverized forms of the two latter. It is prepared artificially by adding ammonium carbonate to a solution of calcium chloride.

Calcium carbonate is almost insoluble in water. Waters containing free carbonic anhydride dissolve it more freely, forming the so-called calcareous mineral waters. They contain, probably, acid calcium carbonate, $CaH_2(CO_3)_2$. This salt has not been obtained in the solid state, because, when these waters are evaporated, they lose a molecule of carbonic anhydride, and yield a precipitate of calcium carbonate. Hence, such mineral waters deposit naturally, on exposure to the air, their calcium carbonate, forming tufa, stalactites, etc., or yield it up upon boiling, forming the incrustations of boilers. Such waters are said to have a "temporary hardness." This hardness is removed by boiling, or by the addition of calcium hydrate in sufficient quantity to form the insoluble normal carbonate.

Exp. 192.—(1) Pass into a solution of calcium hydrate, diluted with an equal amount of water, a stream of carbonic anhydride: calcium carbonate precipitates. (2) Continue the operation, and the calcium carbonate again dissolves. Now divide the product into two parts. (3) Boil one, and observe that it soon becomes turbid. (4) To the other portion add, gradually, a solution of calcium hydrate, and observe the same turbidity, being in both cases due to precipitated calcium carbonate. Upon the latter reaction rests Clark's process of softening calcareous waters.

404. Calcium oxide, CaO, or quicklime, is formed when calcium carbonate is heated to redness in the open air.

It is a white, amorphous, infusible mass. When water is poured upon quicklime, the two combine quickly with great evolution of heat, and the quicklime crumbles to a white powder, which is calcium hydrate: $CaO + H_2O = Ca(HO)_2$. This is the *slaking* of lime. When exposed to the air, quicklime gradually absorbs moisture and forms air-slaked lime. Calcium hydrate dissolves in about 700 parts of cold water to form a feebly alkaline and caustic solution. It readily absorbs carbonic acid, and is used as a test for it.

405. Calcium hydrate suspended in water forms "milk of lime." Its caustic property, together with its strong affinity for carbonic anhydride, renders it a useful agent (1) in tanning, to remove hair from hides; (2) in forming, with fats, insoluble soaps, which are afterward employed in preparing stearine candles; (3) in the preparation of caustic alkalies; (4) in purifying coal gas. (5) When mixed with sand, it is ordinary mortar. This, as it dries, becomes a mixture of calcium carbonate and calcium silicate, capable of binding stones and bricks firmly together. Hydraulic cements, which have the property of hardening under water, contain from 15 to 30 per cent of alumina and silica (clay), and frequently some magnesia. (6) It is also largely used in the manufacture of the "chloride of lime," used in bleaching cotton goods. The process consists simply in passing chlorine gas over slaked lime, whereby a calcium chloride and hypochlorite are simultaneously formed,

$$2\,Ca(HO)_2 + Cl_4 = CaCl_2 + Ca(ClO)_2 + 2\,H_2O;$$

always, however, mixed with an excess of calcium hydrate. This mixture, treated with water, yields an impure solution of calcium hypochlorite, which, when treated with dilute acids, yields either hypochlorous acid or free chlorine, and is, therefore, a powerful bleaching and disinfecting agent.

When this solution is boiled, the chlorate is formed, $3\,Ca(ClO)_2 = 2\,CaCl_2 + Ca(ClO_3)_2$, whence it is economically used in the preparation of potassium chlorate:

$$Ca(ClO_3)_2 + 2\,KCl = CaCl_2 + 2\,KClO_3.$$

406. Calcium chloride, $CaCl_2$, which is a by-product in the last process, is more advantageously prepared for laboratory purposes by the action of hydrochloric acid upon calcium carbonate:

$$CaCO_3 + 2\,HCl = CO_2 + H_2O + CaCl_2.$$

It crystallizes from strong solutions in transparent prisms, $CaCl_2, 6\,H_2O$. These, mixed with snow, form a freezing mixture, reducing the temperature to — 48° C. (more than sufficient to solidify mercury). When heated to 200° C., they become anhydrous; and, on cooling, form a porous mass extremely deliquescent, and therefore largely employed as a desiccating agent in drying gases.

407. Calcium sulphate, $CaSO_4$, is soluble in about 400 parts of water at ordinary temperatures, and about 460 parts at 100° C. Hence, it is not entirely expelled by boiling, and is one of the causes of the "permanent hardness" of water. It is somewhat more soluble in salt waters; but, when these are evaporated, crystallizes out much sooner than the common salt. In nature we find it frequently associated with beds of rock-salt as gypsum and alabaster, $CaSO_4, 2\,H_2O$. When gypsum is heated it loses its water of crystallization; and, if not heated beyond 250° C., retains the power of again uniting with the water, and setting to a hard mass. This calcined gypsum is the "plaster of Paris" used in stucco-work, in making casts, and as a valuable fertilizer.

Exp. 193.—(1) Sift *into* a small quantity of water ground plaster of Paris until it rises to the surface. On stirring this it forms a pasty mass. (2) If, now, this is poured into a suitable mould, it "sets," or hardens, at the same time expanding so as

to fill every cavity of the mould. (3) In a short time it will be so hardened that it can be removed, and will then present an exact reverse copy or cast of the mould. (4) To prevent the cast clinging to the mould, it is only necessary previously to smear it carefully with oil.

408. Calcium phosphate, $Ca_3(PO_4)_2$, is very widely diffused in soils, though not very abundant. It is taken up by plants, especially by cereals, like wheat, and is the chief inorganic constituent of the bones of animals. (See Arts. **227** and **228**).

Compounds of Strontium.

409. Strontium occurs somewhat sparingly in nature as a carbonate, $SrCO_3$ (strontianite), and as a sulphate, $SrSO_4$ (coelestine). These salts are used only as sources of the soluble salts.

The best source of strontium compounds is the carbonate, which is readily soluble in nitric and hydrochloric acids. They are also prepared from the sulphate by (1) roasting it with charcoal, whereby it is converted to a soluble sulphide ($SrSO_4 + 4C = 4CO + SrS$), and (2) dissolving the crude product in hydrochloric or nitric acid, $SrS + 2HNO_3 = H_2S + Sr(NO_3)_2$.

410. Strontium nitrate, $Sr(NO_3)_2$, is readily soluble in water, but is insoluble in alcohol. It is used in fireworks for the preparation of crimson flames. When strongly ignited, it yields *strontium oxide*, SrO, a body similar to quicklime; but, on slaking, is more soluble in water, and yields a more caustic solution. *Strontium chloride*, $SrCl_2$, is freely soluble both in water and alcohol.

Barium Compounds.

411. The principal native compounds of barium are also the carbonate (witherite) and the sulphate (heavy

spar). The sulphate is extensively used as a pigment, under the name of "permanent white," in adulterating white lead, and in the manufacture of paper, to give weight.

Its soluble compounds are obtained like those of strontium.

412. Barium nitrate, $Ba(NO_3)_2$, is insoluble in alcohol, but soluble in 12 parts of cold water. It is used in fireworks to prepare green flames. When ignited, it yields *barium oxide*, BaO, which is soluble in 20 parts of cold water, yielding a strongly caustic solution of barium hydrate, $Ba(HO)_2$. It rapidly absorbs carbonic anhydride from the air, and is used for the volumetric determination of that gas.

413. Barium peroxide, BaO_2, is an interesting compound, prepared by heating barium oxide in a current of air or of oxygen. If, now, the temperature be slightly raised, and steam be passed over the peroxide, oxygen will be given off and barium oxide will remain. It is proposed to prepare oxygen on a large scale by using these reactions alternately. (See Art. **114**).

414. Barium chloride, $BaCl_2$, crystallizes in rhombic, non-deliquescent plates. They are soluble in water, but not in alcohol. Its principal use is in the detection of sulphuric acid.

415. All the soluble salts of barium are poisonous. Any soluble sulphate, as Epsom salts, may be given as an antidote.

416. Tests.—Most of the tests for the metals depend upon the fact that certain reagents, when added to their solutions, form new compounds of sparing solubility.

These new compounds, if *insoluble*, separate out at once; if *difficultly soluble*, at once in strong solutions, but only after a time

in dilute solutions; if *moderately soluble*, only in somewhat concentrated solutions; if *freely soluble*, not until the solutions are so concentrated by evaporation that the point of crystallization is reached.

The delicacy of such reactions, therefore, depends on the insolubility of the new compound formed.

(1) All carbonates, phosphates, and sulphates of the calcium group are either insoluble or difficultly soluble in water. They are formed as white precipitates when any alkaline carbonate, phosphate, or sulphate is added to solutions of their salts.

(2) Calcium sulphate is soluble in 400 parts of water, and its solution may be used for the detection of Ba and Sr. Barium sulphate is quite insoluble, and strontium sulphate nearly so.

(3) Ammonium oxalate also forms a white precipitate with these salts. When free oxalic or acetic acid is present, only calcium oxalate precipitates. This is a very characteristic test for calcium.

(4) Potassium chromate produces an almost insoluble barium chromate, a moderately soluble strontium chromate, and a freely soluble calcium chromate. Hence, a solution of strontium chromate is a characteristic test for barium.

(5) All these salts tinge a colorless flame with a characteristic color: calcium, brick-red; strontium, crimson; and barium, green. When examined by the spectroscope, these colors yield lines of definite refrangibility.

Spectrum Analysis.

417. Most compounds of the alkalies and of the calcium group, are readily volatile. When heated in the almost non-luminous flame of a Bunsen's burner, they yield colored flames which are often sufficiently characteristic to be determined by the eye. If, however, these colored flames are passed through a prism, each flame is found to yield one or more colored lines which have a fixed place in the spectrum, and are therefore characteristic for each element. Upon these facts the spectrum analysis is based.

The spectroscope (Fig. 89) is used for examining colored flames. The substance to be tested is volatilized upon a platinum wire in a Bunsen's burner at E. The flame is passed through a narrow

slit in the tube, A, and thrown upon the prism, P. The light is refracted by this prism in rays of definite refrangibility, which fall upon the object-glass of the telescope, B, and pass through it to the eye. In this way, with a single prism and at moderate temperatures, it is found that sodium yields but one yellow line; lithium, a bright red line and a fainter orange; potassium, two lines—one red and the other violet; thallium, one green line. The spectra of the calcium group are more complex. Strontium yields six red lines, one orange, and one blue line; calcium, several lines, two of which, a green and an orange, are especially characteristic; and barium, a large number of green lines.

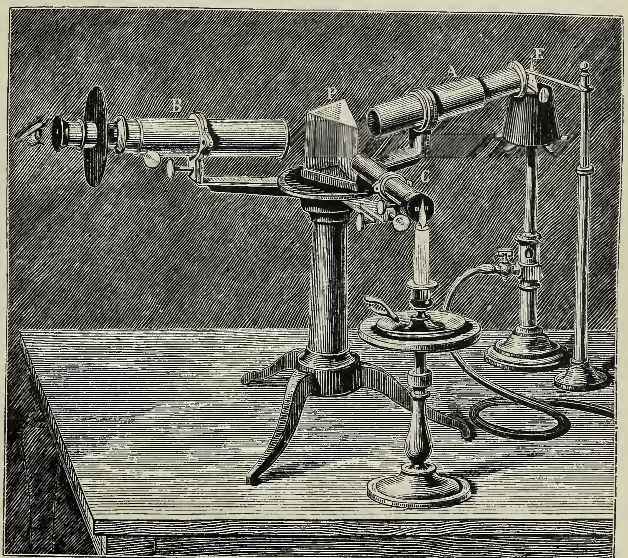


Fig. 89.

In order to fix the place of these lines, a tube, C, is added. It contains at one end a transparent scale of equal parts. When this scale is illuminated by a bright light, it casts a bright image on the prism, which is reflected by the prism into the telescope, B, so that the observer can fix the exact position of the lines produced by the flame which he is examining. In the first scale constructed by Bunsen, the sodium line coincided with the line 50; lithium,

with 31 and 45, etc.* It was also found that these lines were always characteristic, and that, in a mixture, each element yielded its characteristic lines, as if it were volatilized alone. No chemical test rivals this in the delicacy of the reaction. Bunsen calculated that he had found $\frac{1}{180000000}$ of a grain of sodium, and could be certain of $\frac{1}{20000}$ of a grain of caesium.

The method here described is the only one used in the chemical laboratory. It must, however, be added that, at higher temperatures (as that of the electric spark), and by using a train of prisms, other lines are found and other metals volatilized, yielding numerous and characteristic lines.

To the invention of the spectroscope we owe the discovery of caesium, rubidium, thallium, indium, and gallium.

LEAD.

418. Many lead compounds occur in nature, but by far the most abundant is the sulphide, or galena, PbS. The reduction of the sulphide is effected in reverberatory furnaces, in which the dressed galena (1) is roasted at a gentle heat in a current of air. The lead sulphide is thereby converted partly into lead oxide and partly into lead sulphate:

$$PbS + 3O = \widehat{SO_2} + PbO; \quad PbS + 4O = PbSO_4.$$

(2) The furnace is then closed and the temperature raised, whereby the undecomposed sulphide reacts upon the products already formed to produce metallic lead:

$$(1) \quad 2PbO + PbS = \widehat{SO_2} + 3Pb.$$

$$(2) \quad PbSO_4 + PbS = 2\widehat{SO_2} + 2Pb.$$

419. Lead, when freshly cut, is a bluish gray metal, at first lustrous, but soon becoming oxidized. It is very malleable, but of inferior ductility and tenacity; so soft as to leave a streak when rubbed upon paper, and melts at 325° C. Its molten surface, when exposed to the air,

* The scale is arbitrary and differs with each instrument.

rapidly oxidizes to *litharge*, PbO; and, by longer heating, to *red lead*, Pb_3O_4 or $2\,PbO, PbO_2$.

Exp. 194.—Heat dry tartrate of lead in a hard glass tube until the tartaric acid has been decomposed; then cork the tube tightly, and allow it to cool. It contains a mixture of carbon and finely divided lead (*lead pyrophorous*). On pouring this out, it will take fire and burn to litharge.

Hydrochloric and sulphuric acids exert only a surface action upon lead. Its best solvent is nitric acid, somewhat diluted. It is also corroded by acetic acid vapors in the presence of air and moisture. The acetate and nitrate are readily soluble in water, and may be used in forming the insoluble compounds of lead.

420. Lead nitrate, $Pb(NO_3)_2$, crystallizes in octahedra. It is decomposed at a low red heat into oxygen, nitric peroxide, and litharge. Common litharge is an impure, yellow protoxide, obtained in large quantities by the cupellation of silver. Heated for some time below its point of fusion (about 400° C.), it oxidizes further and forms red lead. This oxide, which is sometimes used as a paint, is decomposed by nitric acid,

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + 2\,H_2O + PbO_2,$$

yielding lead nitrate, water, and lead dioxide (PbO_2), the last, a brown powder which is capable of forming salts with both acids and bases. Like many other peroxides, when treated with hydrochloric acid, it evolves chlorine and forms a chloride.

421. Lead chloride, $PbCl_2$, is soluble in 33 parts of water, and forms as a white crystalline precipitate when hydrochloric acid is added to a strong solution of any lead salt.

422. Lead carbonate, $PbCO_3$, is formed as a white precipitate on adding ammonium carbonate to a solution of any lead salt.

The commercial "white lead" is prepared on a large scale by (1) exposing plates of lead in earthen jars to the fumes of vinegar, whereby it is converted into a basic acetate; (2) then burying them in large heaps of tan-bark. This slowly decays, evolving carbonic anhydride, which converts the acetate into a basic carbonate, and (3) sets free the acetic acid to act upon fresh portions of the lead.

White lead has greater opacity, or "body," than the precipitated carbonate, and, when ground with linseed oil, forms the basis of ordinary white paints.

423. Lead sulphide, PbS, occurs native as galena, and may be formed artificially by passing sulphuretted hydrogen through any solution of lead salts. This is a black, amorphous powder, soluble in nitric acid with liberation of sulphur.

424. The soluble lead salts are all poisonous; and, as lead pipes are often used to convey water, it is necessary to consider the action of water upon lead. (1) Pure water free from air does not act upon lead. (2) If the water contains air, the lead oxidizes, forming a slightly soluble hydrate. (3) If, in addition, the water contains chlorides, nitrates, nitrites, or decomposing organic matters, the oxide formed is dissolved, and the water may be seriously contaminated with poisonous lead salts.

On the other hand, (4) if the water contains phosphates, sulphates, and especially carbonates, the hydrate will be changed to an insoluble salt, which protects the lead from further action. Such waters are generally innocuous; but (5) it must be borne in mind that the lead carbonate is slightly soluble in water containing free carbonic anhydride. Hence, (6) when drinking waters are conveyed through leaden pipes, it is safe to use them only when enough has run through to guaranty that they are uncontaminated with lead.

The antidotes for lead poisoning are the soluble sulphates, as

Epsom salts. Weak sulphuric acid is recommended as a prophylactic for workmen engaged in the manufacture of its compounds.

425. The alloys of lead are numerous. Type metal contains about 20 per cent of antimony, and is distinguished not only for its great hardness, but for the sharp casts which it gives, owing to its expansion at the moment of solidification. Soft solder, which melts at 186° C., is an alloy of nearly equal parts of lead and tin. Shot is lead hardened by about two per cent of arsenic.

426. Tests for lead. Lead resembles the metals of the calcium group in the fact that alkaline carbonates, phosphates, and sulphates, when added to solutions of its salts, produce insoluble precipitates. It differs from them in the stability of the metal, its high specific gravity, by the ready reducibility of its compounds, and by the following reactions.

All lead compounds, when mixed with dry sodium carbonate, are readily reduced before the blowpipe, and yield a malleable metallic bead. This bead, dissolved in nitric acid, or any lead salt in solution, yields—

(1) With sulphuretted hydrogen or ammonium sulphide, a black lead sulphide, insoluble in dilute acids;

(2) With hydrochloric acid, a white precipitate soluble in a large excess of boiling water;

(3) With potassium iodide or potassium chromate in neutral solutions, a yellow precipitate.

The Magnesium Group.

427. Magnesium, zinc, and cadmium have many properties in common, and yet present marked differences. They are malleable and somewhat ductile metals which remain unaltered in dry air; but, on being heated, volatilize at high temperatures; and, in the presence of oxygen, burn, forming bulky anhydrous oxides.

These oxides are nearly insoluble in water, but readily combine with acids, forming salts which, in most cases, are isomorphous. Their basic power diminishes with an increase in atomic weights. Magnesium is the most electro-positive of this group. It decomposes boiling water rapidly, while zinc and cadmium act slowly.

On the other hand, magnesium sulphide is decomposed by water; zinc sulphide is soluble in dilute acids (excepting acetic); and cadmium sulphide is insoluble in dilute acids.

It needs also to be remarked that magnesium is related to lithium through the insolubility of its carbonate and phosphate, and to calcium through the isomorphism of their carbonates. All the metals of this group differ from those of the calcium group in the fact that their sulphates are soluble in water.

Magnesium.

428. Magnesium occurs in nature as a carbonate (magnesite). Usually this carbonate is associated with lime, as dolomite ($MgCO_3 + CaCO_3$), or is found in enormous masses as magnesian limestone. It is also found as a silicate in talc, serpentine, and meerschaum. Its soluble salts are widely distributed in mineral waters.

Carnallite is a double chloride of magnesium and potassium, found in large quantities at Stassfurth.

429. The metal magnesium is obtained by fusing its chloride with sodium: $MgCl_2 + 2Na = 2NaCl + Mg$. It is a silver-white metal, which burns in the air with a white flame of dazzling brilliancy. This flame contains enough of the actinic rays to render it serviceable as an artificial light in photography.

430. Magnesium oxide, MgO (*calcined magnesia*), is formed when magnesium is burned in the air, but is

generally prepared by roasting the carbonate. It is a white, bulky, infusible powder, almost insoluble in water, and yet capable, when moistened, of bluing red litmus, forming magnesium hydrate. It gradually changes in the air to magnesium carbonate.

431. Magnesium carbonate, $MgCO_3$. The *magnesia alba* of the druggist is a mixture of magnesium carbonate and magnesium hydrate. It is prepared by adding sodium carbonate to a boiling solution of a magnesium salt, and washing the resulting precipitate. Both the oxide and carbonate are used in medicine as antacids.

432. Magnesium chloride, $MgCl_2$, is formed when hydrochloric acid is added to either of the preceding compounds. Like calcium chloride, it crystallizes with $6H_2O$, and is deliquescent. It can not be deprived of its water of crystallization without decomposition. The anhydrous salt is prepared by igniting the double chloride of magnesium and ammonium: $MgCl_2 + NH_4Cl + 6H_2O$. This first loses its water of crystallization; then the ammonium chloride and the anhydrous magnesium chloride remain.

433. Magnesium sulphate, $MgSO_4 + 7H_2O$ (*Epsom salts*), is a common constituent of mineral waters. It is prepared in considerable quantities from the "bittern" of sea waters, which remains after the sodium chloride has crystallized out; and also from the native carbonate, by treating either with sulphuric acid. It is a very soluble salt, but crystallizes from strong solutions in monoclinic prisms containing seven molecules of water. Six of these molecules are easily driven off by heat, but the seventh is retained even at 200° C. This last atom is the "water of constitution," and may be replaced by various sulphates of other metals, giving rise to double salts with six molecules of water; as,

$$MgSO_4 + K_2SO_4 + 6H_2O.$$

434. All the soluble salts of magnesia have an unpleasant, bitter taste, but many of them are used in medicine as cathartics. All the compounds of magnesia show a strong tendency to combine with the salts of ammonia, and form double salts which are easily soluble in water. Hence, the addition of ammonium salts will very generally hinder the precipitation of magnesium by the ordinary reagents. An exception to this is found in magnesium phosphate.

435. Magnesium phosphate, $MgHPO_4 + 7H_2O$, forms when sodium di-phosphate is added to a magnesium salt. If an ammonium salt is present, a difficultly soluble precipitate of the formula $MgNH_4PO_4 + 6H_2O$ crystallizes out. When this salt is dried and then ignited, it first loses its water, then its ammonia, and becomes changed to magnesium pyrophosphate:

$$2(Mg, NH_4, PO_4 + 6H_2O) = 13H_2O + 2NH_3 + Mg_2P_2O_7.$$

This is the form in which magnesia is generally estimated in quantitative analysis.

Zinc.

436. Zinc occurs in nature chiefly as a sulphide (blende), or as a carbonate (Smithsonite). It also occurs as an oxide (red zinc ore), and as a silicate (calamine).

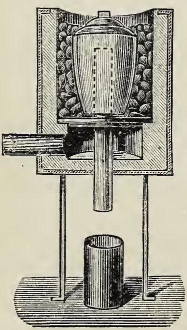


Fig. 90.

In preparing the metal, (1) the ores are roasted in air, whereby they are converted to zinc oxide. (2) This oxide is then mixed with powdered coke and heated in earthen crucibles. At white heat the metal is reduced, and, volatilizing, is condensed in suitable receivers: $ZnO + C = CO + Zn$.

437. Zinc is a bluish-white metal.

It is quite malleable between 100° C. and 150° C., and between these temperatures is readily rolled into sheets. Very curiously, it is brittle both below and above these temperatures, and, in thick plates, breaks with a crystalline fracture. When exposed to the air, zinc soon tarnishes, forming a closely adhering film of oxide, which prevents it from further change. This property is utilized in the so-called galvanized iron, which is iron coated with zinc, to prevent the iron from rusting. Zinc is easily soluble in most acids and in boiling caustic alkalies, with evolution of hydrogen.

$$(1) \quad H_2SO_4 + Zn = ZnSO_4 + \overset{\frown}{H}_2.$$

$$(2) \quad 2KHO + Zn = K_2ZnO_2 + \overset{\frown}{H}_2.$$

In both these cases the action is accelerated by the presence of another metal, as a coil of platinum wire.

Zinc is used as the electro-positive metal in most galvanic batteries, and in the form of sheets for roofing and other purposes.

438. Zinc chloride, $ZnCl_2$, is formed when zinc is dissolved in hydrochloric acid. The solution is used as a disinfectant and in soldering. On evaporating the solution to dryness, a white, deliquescent salt is obtained, which absorbs water greedily, and is sometimes used in surgery as a caustic.

439. Zinc hydrate, $Zn(HO)_2$, is formed when any alkali is cautiously added to a solution of a zinc salt. It is easily soluble in an excess of the precipitant. When dried, it is readily decomposed by heat into *zinc oxide*, ZnO. This body is usually prepared by burning zinc in a current of air. It is a light powder, yellow when hot and white when cold, and extensively used as a paint, under the name of "zinc white."

440. Zinc sulphate, $ZnSO_4 + 7H_2O$, may be obtained by evaporating a solution of zinc in sulphuric acid, as

colorless prisms, isomorphous with magnesium sulphate, which it strongly resembles. It also forms double salts with $6H_2O$; as, $ZnSO_4 + K_2SO_4 + 6H_2O$. It is used in medicine, and produces vomiting when swallowed in even moderate doses.

441. Zinc carbonate occurs native. The precipitate which forms when an alkaline carbonate is added to a zinc solution always contains zinc hydrate, and is a basic carbonate, although its composition varies with the mode of preparation, *e. g.*, $2ZnCO_3 + 3Zn(HO)_2$.

442. Zinc sulphide, ZnS, is formed when zinc salts are decomposed by ammonium sulphide. It is easily soluble in dilute acids (excepting acetic), and is readily oxidized when heated in air. It is the only insoluble white sulphide formed in the wet way, and hence is a characteristic test for zinc.

443. Zinc alloys are numerous and important. Brass contains about one part of zinc to two of copper. German silver contains, in addition, one part of nickel. Many varieties of bronze also contain zinc.

Cadmium.

444. Cadmium is found in small quantities, associated with zinc ores. Being more volatile than zinc, it is obtained from the first portions of the distillate in zinc smelting.

It is a soft, white, easily fusible, and volatile metal. It burns somewhat readily in air, forming a brown oxide, CdO. The metal is used to form alloys, which fuse at very low temperatures. An alloy 8 parts of lead, 15 of bismuth, 4 of tin, and 3 of cadmium, melts at 60° C. (Wood's metal).

Its sulphide is used in water-colors as a yellow pigment. Cadmium iodide is used by photographers.

Tests for the Magnesium Group.

445. In analytical chemistry, these metals are placed in three different groups, because of the behavior of their sulphides.

I. (*a*) In acid solutions, sulphuretted hydrogen precipitates cadmium only as a characteristic, yellow, amorphous powder, insoluble in dilute acids. (*b*) In neutral or alkaline solutions it precipitates white zinc sulphide, which is soluble in all dilute acids, except acetic. (*c*) Magnesium does not form a sulphide in the wet way. If a solution containing these three elements has been treated successively with sulphuretted hydrogen, and ammonium sulphide is mixed with sodium di-phosphate, white $MgNH_4PO_4$ precipitates.

II. The fixed alkalies precipitate all these elements as white hydrates. Zinc hydrate alone is soluble in potash and soda.

III. The alkaline carbonates produce white basic carbonates. The presence of ammoniacal salts either hinders (Cd) or prevents (Mg, Zn) the formation of this precipitate.

IV. Heated before the blowpipe on charcoal, (*a*) magnesium oxide becomes intensely luminous; the residue, moistened with cobalt solution and reheated, yields a pink mass. (*b*) Zinc oxide becomes yellow while hot, and again white on cooling. Moistened with cobalt solution and reheated, it forms a green mass. (*c*) Cadmium oxide, when anhydrous, is a brown powder.

446. Rare dyad metals. To this group are usually referred a number of rare metals which have not been thoroughly classified. Some of these are, perhaps, triads, as their oxides resemble alumina. They have been found only in a few rare minerals, principally obtained in the Scandinavian peninsula.

They are glucinum; thorinum, yttrium, and erbium; lanthanum and didymium; cerium and terbium.

Cerium only has received any practical application. Some of its salts have been used in medicine in various dyspeptic conditions of the stomach.

447. Mercury and copper are metals not easily classified. They form two series of compounds: (1) *ic* salts,

in which they act as dyad elements, as $HgCl_2$, mercuric chloride, and $CuCl_2$, cupric chloride; (2) *ous* salts, in which they are apparently monad elements, as HgCl, mercurous chloride, and CuCl, cuprous chloride.

Theoretically, it is better to consider that these elements are always divalent, and that their *ous* salts contain a double atom of the metal whose affinities partially satisfy each other. Thus the theoretical formula of mercurous chloride is Hg_2Cl_2, and of cuprous chloride, Cu_2Cl_2. These may be represented graphically thus:

$$\begin{array}{l} \mathrm{Hg{-}Cl} \\ | \\ \mathrm{Hg{-}Cl} \end{array} \qquad \begin{array}{l} \mathrm{Cu{-}Cl} \\ | \\ \mathrm{Cu{-}Cl} \end{array}$$

The *ous* salts of both resemble those of silver; the *ic* salts resemble those of the dyad group.

Mercury.

448. Mercury is not widely distributed. It occurs, however, in considerable quantities in a few localities, of which the best known are Idria, in Austria; Almaden, in Spain; and New Almaden, in California. The metal sometimes occurs native, but its principal ore is the sulphide HgS (*cinnabar*), from which it is generally extracted.

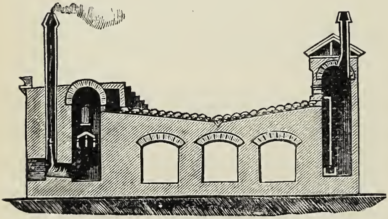


Fig. 91.

The process is very simple. The sulphide heated in air easily decomposes, yielding sulphurous anhydride and mercury:

$$HgS + O_2 = SO_2 + Hg.$$

Sometimes lime is added. The mercury volatilizes and is conducted through earthen pipes, called aludels. The mercury which escapes condensation in the aludels is condensed in large brick chambers.

449. Mercury is the only metal which is liquid at ordinary temperatures. It is largely used in the construction of barometers, and in apparatus for the measurement of gases. It is the most available liquid in the construction of thermometers, because it expands regularly, on being heated, from 0° C. to 100° C. It is solid at —40° C.; volatilizes at all temperatures above 10° C.; and boils at 360° C., yielding a colorless vapor 100 times as dense as hydrogen. It possesses a bright, grayish-white luster, which is scarcely tarnished on exposure to the air. Heated for a long time in air, it forms the red oxide, HgO. It enters into combination with chlorine, bromine, iodine, and sulphur at ordinary temperatures. It decomposes strong boiling sulphuric acid, forming mercuric sulphate; but its best solvent is nitric acid. With this it forms mercurous nitrate, $Hg_2(NO_3)_2$, and mercuric nitrate, $Hg(NO_3)_2$, besides a large number of basic salts.

450. Mercury forms two series of compounds as unlike in their properties as if they had been formed from two different elements. The first series, typified by corrosive sublimate, $HgCl_2$, is the *mercuric* series; the other series, which is typified by calomel, $HgCl$ or Hg_2Cl_2, is the *mercurous* series.

The mercurous compounds are frequently written with half their molecular formulæ; thus, mercurous chloride, or calomel, is represented either by Hg_2Cl_2 or by $HgCl$.

451. The mercurous salts are readily converted by oxidizing agents to mercuric compounds; and the mercuric compounds as easily converted by reducing agents to mercurous compounds.

All compounds of mercury, and even the vapor of mercury, have a decided action when taken in any way into the human system; producing, in excess, a dis-

agreeable and sometimes dangerous salivation. It is, however, curious to note that the mercuric compounds are more energetic in their action, and are deadly poisons. The mercurous compounds are milder, and are more frequently used in medicine.

$$\text{Mercurous Series, } \begin{array}{l} Hg- \\ | \\ Hg- \end{array}$$

452. Mercurous nitrate, $Hg_2(NO_3)_2$, forms when mercury is digested in an excess of cold, dilute, nitric acid. Basic salts form when the mercury is in excess, and mercuric salts, in warm solutions or in strong nitric acid. Mercurous nitrate forms colorless tables, partially decomposed by water, but soluble in water acidified by nitric acid. It is advisable always to add to this solution a little metallic mercury, to prevent the formation of mercuric salts.

453. Mercurous oxide, Hg_2O, is a black, amorphous powder, obtained by adding sodium hydrate to a solution of mercurous nitrate. It is decomposed by heat and light into Hg and HgO.

454. Mercurous chloride, Hg_2Cl_2, or calomel, is a white, amorphous powder, insoluble in water and dilute acids, which may be obtained by adding hydrochloric acid to mercurous nitrate.

Commercially, it is made by subliming (1) a mixture of mercuric chloride and mercury, or (2) a mixture of mercuric sulphate, mercury, and common salt: $HgSO_4 + Hg + 2NaCl = Na_2SO_4 + Hg_2Cl_2$. The vapor is condensed in large chambers, and is then ground to a powder and washed with water. Sodium hydrate decomposes it, yielding black mercurous oxide.

455. Mercurous iodide, Hg_2I_2, is a greenish yellow powder, obtained by mixing solutions of mercurous nitrate and potassium iodide. It is insoluble in alcohol.

MERCURIC SERIES, Hg″.

456. Mercuric oxide, HgO. This has two forms: (1) the red oxide, which is prepared by heating mercury for several days in air at about 450° C.; and (2) a yellow oxide, by adding potassium hydrate to a solution of mercuric salts. The yellow oxide is more susceptible of chemical change, which is perhaps due to the more finely divided state of the precipitated oxide. Either of these forms, on being heated, takes on a darker color, and, at 630° C., decomposes into oxygen and mercury. The residue, if any, becomes red on cooling.

457. Mercuric nitrate, $Hg(NO_3)_2$, is best prepared by dissolving mercuric oxide in an excess of nitric acid. It crystallizes in small needles, which are decomposed by heat, leaving the red oxide.

458. Mercuric chloride, $HgCl_2$ (*corrosive sublimate*). This important salt is obtained usually by subliming a mixture of mercuric sulphate with common salt:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2;$$

for laboratory purposes, by dissolving mercury in aqua regia. It is easily soluble in water and in alcohol, and, on crystallizing, forms rhombohedral prisms which melt at 270° C., and sublime unchanged at 300° C. Its solution has a sharp, metallic taste, and is an active poison. It coagulates albumin, forming with it insoluble "albuminates." Hence, it has been largely used as an antiseptic in preserving animal and vegetable tissues from decay; and hence, also, albumin is an excellent antidote in cases of poisoning by corrosive sublimate.

459. Mercuric iodide, HgI_2, is formed when potassium iodide is added to a solution of mercuric salts. It is first salmon-colored, but changes to a beautiful red precipitate, which is insoluble in water. An excess of either

reagent must be avoided, because very soluble double salts are formed, such as HgI_2KI or HgI_22HgCl_2. If the red iodide is heated, it sublimes in yellow, prismatic crystals, which slowly revert to red octahedra if left untouched, and immediately when rubbed with any hard substance. It therefore exhibits a remarkable example of dimorphism.

460. Mercuric sulphide, HgS, occurs in nature as cinnabar. The artificial sulphide, formed by precipitating mercuric salts with sulphuretted hydrogen, is a black, amorphous powder. When this sulphide is sublimed, or when mercury is sublimed at a low red heat with one-sixth of its weight of sulphur, a beautiful red sulphide forms, which is the pigment known as *vermillion.*

461. Ammonium compounds of mercury are formed when ammonia or its salts act upon the compounds of mercury. They may be regarded as derived from ammonium, in which two atoms of hydrogen are replaced by a double mercurous atom $(N^vH_2Hg'_2)'$, or by the mercuric atom $(N^vH_2Hg'')'$. In either case, a monatomic radical is formed, which may combine with any negative monatomic radical; or, in multiple forms, with dyads, triads, etc. These compounds are very numerous.

Among the most important are:

(1) *Di-mercurosum-chloride* (NH_2Hg_2Cl), which forms as a black powder when calomel is treated with aqua ammonia, and becomes gray upon drying:

$$Hg_2Cl_2 + 2\,NH_4, HO = \underbrace{NH_2Hg_2Cl}_{} + NH_4Cl + 2\,H_2O.$$

(2) *Mercuric ammonium chloride* (NH_2HgCl), commonly known as "white precipitate," which forms when an excess of aqua ammonia is added to a solution of mercuric chloride:

$$HgCl_2 + 2\,NH_4, HO = NH_4Cl + 2\,H_2O + NH_2HgCl.$$

When the mercuric chloride is in excess, a double salt forms,

$NH_2HgCl + HgCl_2$; but, if ammonium chloride is in excess, a "fusible white precipitate," $NH_2HgCl + NH_4Cl$.

In like manner, iodides, bromides, nitrates, sulphates, etc., may be formed, containing either NH_2Hg_2 or NH_2Hg'' as the positive radical.

462. The alloys of mercury are called *amalgams.* The metals of the alkalies, gold, silver, zinc, tin, lead, and bismuth dissolve readily in an excess of mercury. When the excess of mercury is removed, these amalgams are frequently solid, and have received important applications in the arts. Sodium amalgam is used for extracting gold and silver from their ores; tin amalgam is used for silvering mirrors; an amalgam of tin and silver, for plugging hollow teeth.

TESTS.—(1) All solid compounds of mercury yield, when mixed with dry sodium carbonate and heated in a test tube of hard glass, globules of metallic mercury.

(2) Solutions of the salts of mercury are reduced by copper, forming upon it a white metallic coating, with a greasy feel.

(3) Mercurous compounds give black precipitates with the alkalies and with sulphuretted hydrogen; with hydrochloric acid, a white precipitate of calomel.

(4) Mercuric compounds give, with caustic soda or potash, a yellow precipitate; with sulphuretted hydrogen, a black precipitate (at first white); with potassium iodide, a red precipitate.

COPPER.

463. Copper sometimes occurs native, generally massive, but, at times, in octahedral crystals. More frequently it is found as a sub-oxide (red copper ore), or as a carbonate (malachite). Its principal ore is the sulphide (copper pyrites), although this is seldom found pure, being largely associated with iron, and frequently with other elements, as arsenic and antimony.

464. The preparation of copper from its native form or from its oxygen compounds requires merely the

smelting of the ore with coal. The reduction of copper from the sulphide is a more complex process.

(1) The ore is first roasted in a reverbatory furnace (Fig. 80), whereby certain constituents (As, Sb, S) are volatilized, and others oxidized (FeS_2 to Fe_2O_3). (2) This product is roasted with a mixture of coal and silicates, to produce a soluble *slag* with the iron, while the copper accumulates as a nearly pure sub-sulphide (Cu_2S). (3) When the iron has been removed by a succession of these operations, the heat is raised and a portion of the copper is oxidized and reacts upon the remaining sub-sulphide ($2\,CuO + Cu_2S = SO_2 + 4\,Cu$), yielding metallic copper. (4) The final stage of the process consists in stirring up the melted mass with a long stick of green wood, which reduces the last portions of the oxide. The metal is then drawn off and cast into ingots.

465. Copper is a reddish metal, very malleable, ductile, and tenacious, and is one of the best conductors of heat and electricity. It preserves its brilliant luster unchanged in dry air, unless heated, when it oxidizes rapidly, forming a many-colored film, which finally changes to scales of the black oxide. In moist air it becomes dull looking, and slowly forms a crust of green basic carbonate. This change takes place more rapidly in the presence of acid vapors, or when the copper is moistened with ammonia or with solutions of chlorides.

466. It is a dyad which differs from all those previously studied in its high melting point (1200° C.), and in the fact that it is only slightly volatile, even at very high temperatures. It resembles mercury in some of its properties: (1) in that it is hardly attacked by hydrochloric or sulphuric acid, except when heated, but readily dissolves in dilute nitric acid; (2) by forming ammonium compounds in which the copper apparently replaces a part of the hydrogen of the ammonium, as $2NH_3, CuCl_2$; and (3) in forming two series of salts—the cuprous, typified by cuprous chloride (Cu_2Cl_2), and the cupric, typified by cupric chloride ($CuCl_2$). The

latter series is by far the most abundant and important of the copper compounds.

467. Cuprous chloride, Cu_2Cl_2, is best made by digesting for some time a mixture of copper filings and cupric oxide in hydrochloric acid. The salt is soluble in hydrochloric acid; but, when the solution is poured into a large quantity of water, it separates out as a white crystalline powder.

468. Cuprous oxide, Cu_2O, is obtained when a solution containing cupric sulphate, grape sugar, and an excess of sodium hydrate, is warmed. Generally, a yellow cuprous hydrate, Cu_2O, H_2O, first separates out; but, on longer boiling, anhydrous red cuprous oxide is formed. This reaction is facilitated by a considerable addition of tartaric acid. The red oxide is used to impart a beautiful ruby color to glass.

Most oxy-acids decompose this oxide, precipitating metallic copper and forming cupric salts.

469. Cupric oxide, CuO, may be prepared by roasting copper in air or by igniting the nitrate. When sodium hydrate is added in excess to a solution of a cupric salt, a pale blue precipitate forms, which is cupric hydrate, $Cu(HO)_2$; but, upon heating the mixture, the black anhydrous oxide forms, even in the presence of water. It is easily reduced, especially in the presence of hydrocarbons, for which reason it is extensively used as an oxidizing agent in organic analyses.

Combined with oxy-acids, it forms a large series of salts, which are all white when anhydrous, and blue or greenish when hydrated.

470. The native sulphide, CuS, has already been mentioned as one of the chief sources of copper. It is formed artificially as a black precipitate when sulphuretted hydrogen is added to cupric solutions. It is readily oxidizable in air, forming cupric sulphate.

471. Cupric sulphate, $CuSO_4 + 5H_2O$ (*blue vitriol*), is the most important salt. It is obtained on boiling copper in strong sulphuric acid, as blue triclinic prisms:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

These crystals are changed to a white anhydrous powder at about 200° C., which absorb water greedily, and again become blue. Hence, it is used to remove the last portions of water from alcohols, ethers, etc. Although it contains but $5H_2O$, it forms with alkaline sulphates double salts containing $6H_2O$, and therefore analogous, as they are isomorphous with magnesium double sulphates; *e. g.*, $K_2, Cu(SO_4)_2 + 6H_2O$. With an excess of aqua ammonia, it forms an exceedingly soluble blue compound ($4NH_3$, H_2O, $CuSO_4$), which, upon being dried and heated to 150° C., becomes cupric-ammonium sulphate, $2NH_3, CuSO_4$.

472. Cupric nitrate, $Cu(NO_3)_2$, is made by dissolving copper in nitric acid. On evaporating, bright blue crystals form, which are very deliquescent and easily decomposed by heat, leaving cupric oxide.

473. Numerous carbonates of copper occur in nature. The most prized of these is malachite, which takes a high polish and is used for ornaments. A similar compound forms when sodium carbonate is added to a hot solution of a cupric salt, $CuCO_3 + Cu(HO)_2$.

474. The uses of copper in the arts are well known; but, perhaps, its alloys are more extensively used than the metal itself. Gun metal, bell metal, bronze, and speculum metal are alloys with tin, containing from 66 to 90 per cent of copper. They are distinguished by great hardness, and a susceptibility of taking on a high polish. Copper is also a constituent of brass, German silver, most alloys of silver, and of "red" gold.

The sulphate of copper is largely used in galvanic

batteries and in electrotyping. Some of the salts of copper are valuable pigments. Brunswick green is an oxy-chloride. Scheele's, or Paris, green and Schweinfurt green are arsenites; beautiful greens, but very poisonous. Verdigris is a basic acetate, although this term is often incorrectly applied to the green basic carbonate which forms when copper is exposed to moist air.

It must not be forgotten that all soluble salts of copper are *active poisons.* Too much care can not be taken to keep copper vessels used for cooking perfectly bright and clean, as the presence of oily matters facilitates the solution even of the black oxide. Its proper antidote is the albumen of eggs.

Tests.—(1) Ammonia, added to any cupric solution, produces at first a greenish blue precipitate which dissolves in excess, forming an azure blue solution. (2) Potassium ferrocyanide gives a dark brown precipitate of cupric ferrocyanide. (3) Sulphuretted hydrogen, or an alkaline sulphide, forms a black precipitate insoluble in dilute acids and slightly soluble in ammonia. (4) A bright slip of iron plunged in an acid solution of copper, even when quite dilute, becomes soon coated with the red metal. (5) See § 758.

Recapitulation.

Review §§ 400, 401; 427; 447.

These dyad elements may be arranged with the monads Li and Ag into sub-groups, as follows:

I		II		III	
Calcium,	40	(Li. 7)		Copper,	63
Strontium,	87.5	Magnesium,	24	(Ag 108)	
Barium,	137	Zinc,	65	Mercury,	200
Lead,	204	Cadmium,	112	Lead,	207

Their carbonates are insoluble in H_2O, and are decomposed by heat, yielding oxides.

The oxides of the first sub-group resemble those of the alkalies, BaO being the nearest.

The chlorides of the first and second sub-groups are all soluble in water, and most are deliquescent bodies.

The protochlorides of the third sub-group are either insoluble in water or difficultly soluble (Pb in 33 parts).

CHAPTER XIII.

THE TRIAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	MELTING POINT. °C.	DISCOVERER.
Indium	In	113.4	7.4	176°	Reich and Richter, 1863.
Gold	Au	197	19.34	1250°	
Thallium	Tl	204	11.8	285°	Crookes, . . . 1861.

475. These metals have few properties in common, beyond the fact that they are triad elements, uniting with three atoms of chlorine to form $InCl_3$, $TlCl_3$, and $AuCl_3$.

Indium and thallium are very rare. The principal interest that attaches to them is derived from the fact that they were recently discovered by the application of the spectrum analysis. The spectrum of indium contains two bright blue bands. It occurs in some ores of zinc, which metal it very much resembles. Thallium is more widely distributed, though in very small quantities. Its principal sources are certain iron and copper pyrites. In its physical properties it resembles lead; but, in its chemical, is more closely allied to the alkalies, forming a caustic hydrate, TlHO, and to silver, forming an insoluble white chloride, TlCl.

Gold.

476. Gold is more widely distributed than is generally supposed, being found in many alluvial sands in all parts of the world. Its richest deposits are in California and Australia. It is generally found native, but is frequently associated with ores of other metals. It is obtained (1) by simple washing in a stream of water, or (2) by treating the crushed ore with mercury, which dissolves out the gold. The resulting amalgam is distilled, the mercury is recovered for future operations, and the gold which remains is cast into bars.

477. Gold is a yellow metal, of high specific gravity, very malleable and very ductile. When obtained in very thin sheets, it transmits a green light. It is so soft that pieces of pure gold foil may be welded together by pressure, as in dentistry. The gold used in coins or for ornaments is hardened by being alloyed by copper or by silver.

An ancient commercial method of measuring the fineness of gold still obtains: pure gold is reckoned at 24 carats; and the alloys are said to be as many carats fine as they contain parts of gold in 24. Thus, the best jewellers' gold is 18 carats fine, and contains $\frac{18}{24}$ of its weight in gold. One U. S. gold dollar weighs 25.8 grains, and contains 90 per cent of gold (21.6 carats fine). At this rate, pure gold is $20.67 per Troy ounce. British coin is 22 carats fine.

478. Gold is not acted upon by air, by water, or by ordinary acids. It, however, dissolves readily in any liquid which contains free chlorine. Aqua regia is its best solvent, yielding *auric chloride.*

479. Auric chloride, $AuCl_3$, on evaporation forms a red deliquescent mass. With alkaline chlorides it forms yellow, needle-like crystals; as, $NaAuCl_4 + 2\,H_2O$. The commercial chloride has the formula $AuCl_3, HCl$. Heated to about 150° C., it partially decomposes, leaving *aurous chloride,* a white powder insoluble in cold water.

480. Auric oxide, $3H_2O, Au_2O_3$, forms when auric chloride is digested with magnesia. It possesses no basic properties, but rather acts as a weak acid. It dissolves in excess of potassium hydrate, and, on evaporating, yields yellow needles: $K_2O, Au_2O_3 + 3H_2O$.

Aurous oxide, Au_2O, acts as a feeble base. Its only important salt is made by mixing solutions of auric chloride and sodium hyposulphite. It is a double hyposulphite of gold and sodium: $Na_3Au, 2S_2O_3 + 2H_2O$. It is used by photographers in "toning"; and, very curiously, neither ferrous sulphate nor stannous chloride serves to detect gold in its solution.

481. The uses of gold in coinage and in ornaments have been known through all ages of the world. In recent times, it has been largely employed in gilding, especially by the application of galvanism. The gold is usually deposited from a solution of the cyanide, $Au(CN)_3$, and may be obtained in any required thickness. Gold, in its finely divided state, as in the purple of Cassius, is used to impart a ruby color to glass, and for gilding porcelain.

TESTS.—(1) All gold compounds are readily reduced to metallic gold by heating.

(2) Gold is also easily reduced in solutions not containing free nitric acid by ferrous sulphate, by oxalic acid, and by many other reducing agents in the form of a brown powder.

(3) Stannous chloride produces a purple precipitate (purple of Cassius), which is, perhaps, Au_2O, SnO, SnO_2.

CHAPTER XIV.

THE TETRAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	DISCOVERER.
Osmium	Os	199	22.47	Tennant, 1803.
Ruthenium	Ru	104.4	11.4	Klaus, 1844.
Iridium	Ir	198	21.1	Tennant, 1803.
Rhodium	Rh	104.4	12.	Wollaston, 1804.
Platinum	Pt	197.5	21.5	Wood, 1741.
Palladium	Pd	106.6	11.8	Wollaston, 1803.
TRIAD AND MONAD METALS.				
Gold	Au	197	19.3	Known from earliest times.
Silver	Ag	108	10.5	

482. These metals are popularly classed together as the "noble metals." They possess many properties in common, viz: a remarkable power of resisting oxidation and of retaining their luster unchanged in air; a high fusing point; large atomic weights; and high specific gravities. It will be observed that in the table they are arranged in pairs. The two members of each more strongly resemble each other than they do the other

members of the group, although their atomic weights and specific gravities bear nearly the proportion of 1 : 2.

Gold and silver, which we have already studied, agree in forming an insoluble monad chloride, and soluble double salts with the alkaline chlorides. They differ in their fusing points, in specific gravity, and in the power of resisting oxidation. Somewhat similar relations and differences are found in the other pairs of the group, especially between platinum and palladium; but we must not attempt to form a strict parallelism. Iron resembles osmium because of its acid anhydride FeO_3; and nickel, palladium because it has but one basic oxide.

483. The first six metals of the table are tetrad metals, known as the platinum group. Though sometimes found native, these more frequently occur as alloys containing from two to four of the metals; as, for example, palladium is generally found with platinum. Iridium, rhodium, and osmium also occur with platinum; while iridosmine (a very hard mineral used for the points of gold pens) generally consists of iridium, osmium, rhodium, and ruthenium.

484. Osmium and ruthenium are white, brittle metals, nearly or quite infusible in the oxy-hydrogen blowpipe. Nevertheless, osmium is somewhat volatile, and both differ from the other metals of this group in combining with oxygen in the air at high temperatures. Their highest oxides are OsO_4, RuO_4, which are the only tetroxides known, and are neutral bodies of offensive odor, combining neither with bases nor acids. Their tri-oxides act as acids. They form, in all, five oxides; as, OsO, Os_2O_3, OsO_2, OsO_3, OsO_4; and three chlorides; as, $OsCl_2$, Os_2Cl_6, and $OsCl_4$. These, however, are not of sufficient importance to warrant further notice.

485. Iridium and rhodium are grayish-white metals, hard and brittle, and with difficulty fused in the oxy-

hydrogen flame. When pure, they are not soluble, even in aqua regia, but may be oxidized by fusion with niter. Iridium forms three chlorides: $IrCl_2$, Ir_2Cl_6, and $IrCl_4$. Only one chloride of rhodium is known—Rh_2Cl_6; but an oxide, RhO_2, is known.

486. Platinum and palladium are the most abundant of the members of this group. They are also more nearly related, being both brilliant white metals, fusible only in the oxy-hydrogen flame, quite malleable and ductile, and possessing considerable tenacity. In all these respects palladium is the inferior metal, but it surpasses platinum in hardness.

Both form two chlorides: $PtCl_2$, $PtCl_4$, and $PdCl_2$, $PdCl_4$, and the corresponding oxides; that is, they act both as bivalent and quadrivalent elements.

487. Palladium is the only metal of the group which is soluble in HCl, H_2SO_4, and in HNO_3. The nitrate, $Pd(NO_3)_2$, is used for the quantitative determination of iodine, forming, when added to solutions of iodides, a black precipitate of PdI_2.

488. The metal palladium possesses the curious faculty of absorbing, or "occluding," about 900 times its volume of hydrogen. This product is sometimes regarded as an alloy of palladium with hydrogen. It is a stronger reducing agent than hydrogen itself, easily reducing $HgCl_2$ to Hg_2Cl_2, and finally to Hg.

489. The metal platinum, in a state of fine division (spongy platinum or platinum black), absorbs more than 200 times its volume of oxygen, and then acts as a strong oxidizing agent, being capable of converting alcohol to acetic acid, and of setting on fire a stream of hydrogen.

490. Platinum tetrachloride, $PtCl_4$, is the only important salt of platinum. It is obtained as a yellow, ex-

tremely deliquescent mass when platinum is dissolved in aqua regia. Its principal use is to form double chlorides with alkaline chlorides. All of these, except that with sodium, are difficultly soluble in water and alcohol. Hence, platinum tetrachloride is a valuable reagent in the quantitative determination of the alkalies, except sodium.

491. The double chloride, $PtCl_4, 2NH_4Cl$, when heated to redness, is entirely decomposed, yielding the "spongy platinum" above referred to. Platinum black is platinum in a still finer state of division, obtainable by heating a mixture of solutions of sugar, sodium carbonate, and platinum tetrachloride. It is used as a coating on the silver plate in Smee's battery.

492. Platinum is the only metal of this group which has received any extensive applications in the arts. It is especially valuable for crucibles, sulphuric acid stills, and in the wires used for electric fuses. It was for a time used in Russia for coins, but was not found convenient.

TESTS.—(1) All dry salts of the platinum group are reduced by heat alone, frequently to spongy masses; all infusible, except by the oxy-hydrogen blowpipe.

(2) All solutions of the salts of these metals are precipitated as brown or black sulphides by H_2S. Of these the sulphides of platinum and iridium are soluble in ammonium sulphide.

Recapitulation.

The noble metals are difficultly fusible, and are not easily acted upon by acids.

$PtCl_4$ forms difficultly soluble double salts with most of the alkaline chlorides.

Ag, Au, and Pt alone find extensive employment in the arts.

CHAPTER XV.

THE HEXAD GROUP OF METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	DISCOVERER.	
Nickel	Ni	58.7	8.82	Cronstedt,	1751.
Cobalt	Co	59	8.95	Brandt,	1733.
Iron	Fe	56	7.84		
Manganese	Mn	55	8	Scheele,	1774.
Chromium	Cr	52.2	6.81	Vauquelin,	1797.
Aluminium	Al	27.4	2.6	Woehler,	1828.
Gallium	Ga	69.9	5.93	Lecoq de Boisbaudran,	1876.
Molybdenum	Mo	92	8.62	Hielm,	1782.
Tungsten	W	184	17.6	d'Elhujar,	1781.
Uranium	U	240.	18.3	Klaproth,	1789.

493. Molybdenum and tungsten resemble each other, but differ in most respects from the remaining metals given in the table. They are rare elements imperfectly studied, and are probably hexad, as shown by the chlorides, MoO_2Cl_2, WCl_6, and the anhydrides, MoO_3, WO_3. They also form a variety of complex products. The only compound of importance is ammonium molybdate, $(NH_4)_2O, MoO_3$, which is used in precipitating phosphoric and arsenic acids from acid solutions.

494. Uranium is a rare metal which, in its analytical reactions, somewhat resembles iron. Its nitrate has the formula $UO_2(NO_3)_2$, and is a yellow, crystalline salt, easily soluble in water. When heated, it leaves a residue of yellow U_2O_3, which, when further ignited, becomes brown UO_2. When treated in solution with sodium hydrate, it precipitates as uranium hydrate, $UO_2(OH)_2$, a yellow body capable of acting both as an acid and as a base. The group $(UO_2)''$ is called *uranyl*, a diatomic radical, which is an unusual form. This radical appears in many of its compounds, as UO_2Cl_2, and in its most usual mineral, $UO_2, 2\,UO_3$. Uranium is used in the determination of phosphorus by volumetric analysis, forming in solutions of phosphoric acid salts an amorphous yellow precipitate, insoluble in acetic acid, of the formula $(UO_2)''HPO_4 + 4\,H_2O$. The oxides of uranium are used in preparing a greenish yellow glass.

495. The other elements given in the table are frequently classed together as the "iron group." Those that are arranged in pairs often show striking resemblances; but it can not be said that the group as a whole is so definitely characterized as several of those which have been already studied.

The one particular in which they all agree is in the formation of a sesqui-oxide, R_2O_3; and all except nickel have the corresponding hexachloride, R_2Cl_6. If we admit the double atom R_2, these elements are tetratomic or hexatomic,

$$\text{as,}\quad \begin{array}{c} Fe{\equiv}Cl_3 \\ | \\ Fe{\equiv}Cl_3 \end{array} \quad \text{or} \quad \begin{array}{c} Fe{\equiv}Cl_3 \\ ||| \\ Fe{\equiv}Cl_3 \end{array} \quad \text{and} \quad \begin{array}{c} Al{\equiv}Cl_3 \\ | \\ Al{\equiv}Cl_3 \end{array} \quad \text{or} \quad \begin{array}{c} Al{\equiv}Cl_3 \\ ||| \\ Al{\equiv}Cl_3 \end{array},$$

in these compounds. Admitting only the single atom, and writing the formula $AlCl_3$, they are apparently triad. Some chemists prefer to reckon aluminium only as a triad, since it forms only this series of com-

pounds. Nevertheless, it is closely related to chromium and to iron. Chromium forms an undoubted hexad, CrF_6; and probably in the higher oxides, CrO_3, FeO_3, MnO_3, chromium, iron, and manganese are hexads. With the exception of aluminium, all the members of the group also act as dyads; as, $NiCl_2$, $FeCl_2$. Nickel forms only this series of salts, and the dyad salts of the other elements are quite stable. The dyad oxides are all strong bases, forming salts which resemble those of zinc and magnesium, with which, also, they are isomorphous, and, like them, form double sulphates with the alkalies; as, $K_2Fe(SO_4)_2 + 6H_2O$.

496. The tetrad oxides, Fe_2O_3, Cr_2O_3, Al_2O_3, Mn_2O_3, are weak bases, forming with alkalies double sulphates which are alums; as, $Al_2O_3, 3SO_3 + K_2O, SO_3 + 24H_2O$ or $AlK(SO_4)_2 + 12H_2O$. The sesquioxide of aluminium acts also as an acid, forming with the alkalies aluminates as, K_2O, Al_2O_3, or $KAlO_2$.

The hexad oxides are acid anhydrides, forming salts like K_2O, CrO_3 and K_2O, MnO_3.

497. It will be noticed that in the table on page 192 manganese is placed among the heptad elements. Manganese forms a fluoride MnF_7, and is probably septivalent in the permanganates; as, K_2O, Mn_2O_7 or $OK\text{–}Mn\equiv O_3$.

Nickel and Cobalt.

498. These elements are strikingly similar. They generally occur together in nature, being found native in meteoric iron, but more frequently as sulphides or arsenides, associated with other metals. The process of extracting the nickel and cobalt from these ores is very complicated. From the oxides, the metals are obtained by roasting with charcoal at white heat; or from the oxalates, by simple ignition. The oxalic acid decom-

poses, yielding carbonic oxide, which reduces the remaining oxide. Cobalt is the less abundant, and is not produced in the metallic state on a large scale. Nickel has quite an extensive use in certain alloys, as German silver, and in small coins; and recently has been employed in nickel-plating, to protect steel instruments from rusting.

499. Both metals resemble iron in their physical properties. They are white, hard, malleable, and tenacious metals, the tenacity of cobalt even exceeding that of iron; and are also strongly magnetic, but less so than iron. They resist oxidation in moist air, and are not easily soluble in either hydrochloric or sulphuric acids. Their best solvent is nitric acid.

500. Both form a stable series of salts, in which they act as divalent metals. The hydrated salts of nickel are generally green, but yellow when anhydrous; those of cobalt are generally rose-red when cold, but on heating, blue, becoming anhydrous.

501. The most important salt of nickel is *the sulphate*, $NiSO_4\,7H_2O$, which forms crystals isomorphous with those of magnesium sulphate. It also forms with alkaline sulphates double salts; as, $K_2Ni(SO_4)_2 6H_2O$.

On adding caustic soda to a solution of the sulphate, an apple-green hydrate, NiO, H_2O, precipitates, which is easily soluble in acids. From this may be prepared nickel chloride, $NiCl_2$, by the addition of hydrochloric acid. On adding sodium carbonate or oxalic acid to a moderately concentrated solution of the sulphate, bluish-green precipitates form, which are respectively carbonates or oxalates of nickel.

502. The most important salt of cobalt is *the nitrate*, $Co(NO_3)_2 + 6H_2O$, a deliquescent, very soluble, rose-red salt. Its solution treated with sodium hydrate yields CoO, H_2O, which is at first blue and then changes to

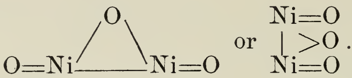
rose-red. Either the hydrate or the nitrate, when heated, changes to the brown anhydrous sesqui-oxide Co_2O_3. This is an important agent in blowpipe analysis. It yields, when ignited with various other oxides, residues of characteristic colors, viz: with magnesia, a pink mass; with zinc, a green mass; and with alumina, a blue mass. Still more remarkable is the magnificent blue which it communicates to borax or to alkaline silicates. These reactions have also been used in the arts upon a large scale to produce pigments such as Rinman's green (with ZnO) and Thenard's blue (with Al_2O_3), for imparting a sapphire-blue color to porcelain glaze, and for making blue glass. *Smalt* is blue glass ground to a fine powder and washed.

503. Cobaltic nitrite. If to a strong solution containing cobalt, a strong solution of potassium nitrite is added, and then enough acetic acid to liberate the nitrous acid, all the cobalt, upon standing, is precipitated as a difficultly soluble yellow powder (Co_2O_3, $3K_2O$, $5N_2O_3$). Nickel does not form a corresponding salt, and hence this difference in reaction is one of the means used to separate the two elements.

504. Cobaltous chloride, $CoCl_2$. is obtained in red prisms containing $6H_2O$, by dissolving either the oxide or the carbonate in hydrochloric acid. If a drawing is made with its dilute solution upon paper, it is nearly colorless; but, when heated to about 150°, it becomes anhydrous and appears as a bright blue, which again disappears in moist air. This property has led to its use in a so-called chemical hygrometer, and in sympathetic inks.

505. Both nickel and cobalt, when their dyad solutions are mixed with ammonia, yield a hydrate which dissolves in excess of ammonia. The solution contains a double

salt of ammonia and the salt of nickel or cobalt used. If, now, chlorine gas be passed into either solution, a black precipitate forms which is the hydrated sesquioxide, $Ni_2O_33H_2O$ or $Co_2O_33H_2O$. The same precipitate forms when an alkaline hypochlorite is added to either hydrate in the presence of free alkali. In these sesquioxides both metals act as tetrads; thus:



Nickel forms no other tetravalent compounds.

506. Cobalt forms, as a tetravalent element, several salts, among which those with ammonia and cyanogen are the best known.

(1) If the solution of cobaltous hydrate in ammonia is exposed to the air, it gradually absorbs oxygen to form cobaltic compounds (of Co_2O_3) with ammonia. These compounds are very numerous and of complex constitution. They may be very generally regarded as ammonium compounds, in which the double atom of cobalt has replaced two or more hydrogen atoms of ammonium. The roseocobaltic chloride has the formula $Co_2Cl_6, 10H_3N + 2H_2O$.

(2) If to a solution of a dyad salt of nickel or of cobalt, potassium cyanide in solution is cautiously added, the cyanides, $NiCy_2$ (greenish) or $CoCy_2$ (brownish), precipitate. Both dissolve in an excess of the potassium cyanide. The nickel double cyanide suffers no further change. Freshly precipitated mercuric oxide precipitates from this solution nickel oxide completely. If, however, the cobaltous double cyanide is exposed to the air, it forms the potassium cobalti-cyanide, from which the cobalt is not precipitated by mercuric oxide nor by ordinary reagents. The cobalt in this is probably hexavalent, thus:

$$\begin{array}{l} K_2Cy_3\text{—}Co{<}Cy_3K \\ \qquad\quad\ \ \vert\vert\vert \\ K\ Cy_3{>}Co\text{—}Cy_3K_2 \end{array} \quad \text{or} \quad K_6, Co^{VI}{}_2, 4Cy_3.$$

This difference of reactions affords the most accurate method of separating nickel from cobalt.

507. It remains only to notice a very curious phenomenon. When to a solution of calcium hypochlorite a few drops of cobaltous nitrate are added, the black sesquioxide immediately precipitates. If, now, the solution is heated to 80° C., oxygen will be given off until all the hypocholorite is changed to calcium chloride.

A very small quantity of the Co_2O_3 is capable of decomposing an unlimited quantity of the hypochlorite, CaO, Cl_2O to $CaCl_2 + O_2$. The alleged reaction is that the hypochlorite changes the Co_2O_3 to CoO_3, a body which is unstable at boiling heat, two molecules decomposing to O_3 and Co_2O_3, and thus becoming capable of removing more oxygen from the hypochlorite.

Tests for Nickel and Cobalt.—(1) Their dry compounds, mixed with sodium carbonate and heated in the reducing flame before the blowpipe, yield a magnetic powder.

(2) If this powder yields a blue borax bead in the oxidizing flame, which is also persistent in the reducing flame, cobalt is present.

(3) Cobalt is precipitated by potassium nitrite, while nickel is not.

(4) They are best separated by their reactions with cyanogen; but this process is too dangerous to be used except by trained chemists. The cobalt forms a cobalti-cyanide; the nickel forms no corresponding salt.

Iron and Manganese.

508. These metals are also closely related in most of their physical and chemical properties, and are frequently associated together in nature. They act as positive elements in two series of salts: (1) a stable dyad "*ous*" series, correspondent in formula and frequently isomorphous with those of the magnesium group, as $FeCl_2$, $MnSO_4$; (2) a stable tetrad "*ic*" series, containing a double atom in which they are quadrivalent, although apparently trivalent, as $Cl_3{\equiv}Fe{-}Fe{\equiv}Cl_3$ or Fe_2Cl_6. The sulphates form, with alkaline sulphates,

alums which are isomorphous with those of the next group, as $K_2O, SO_3 + Fe_2O_33SO_3 + 24H_2O$.

They act also as negative elements, forming salts like K_2MnO_4, which are isomorphous with chromates, as K_2CrO_4. They form, therefore, a connecting link between the pairs of this group.

509. Iron is found native in meteorites, which are sometimes so pure that they can be wrought. In small quantities, its compounds are found every-where; and it is also abundantly found in numerous and thickly distributed mines, which have sometimes almost the dignity of mountains, as in Michigan, Wisconsin, and Missouri.

It is so abundant that its sulphides, arsenides, and other ores difficult of reduction have no commercial value as sources of iron. The reducible ores are its various oxides and carbonates; and these are worked only when found in considerable quantities.

510. The principal of these useful ores are: magnetite, Fe_3O_4 (Fe, 72 per cent); hematite, with its varieties, clay iron stone, specular iron, etc., Fe_2O_3 (Fe, 70 per cent); spathic iron, $FeCo_3$ (Fe, 48 per cent); and black band, a carbonate associated with carbonaceous matters. The working value of an ore frequently depends on the mineral deposits with which it is associated, as coal and lime. One of the best ores of Ohio is a carbonate containing about 40 per cent of iron.

511. These oxy-compounds, if pure, are easily reduced to the metallic state (wrought iron) by smelting with coal. A few so-called "bloomery forges" are now in operation in the United States, producing wrought iron directly from the ore. Generally speaking, the mineral matters with which the ore is mixed require to be separated, and the smelting process becomes more complicated.

The Ordinary Manufacture of Iron.

512. The first stage consists in making *cast iron.* This is effected in tall blast-furnaces, whose shape will be understood from the figure. It is, however, necessary to add that the pipes, t, at the base are called *tuyeres*, through which a blast of cold or of hot air may be driven into the stack.

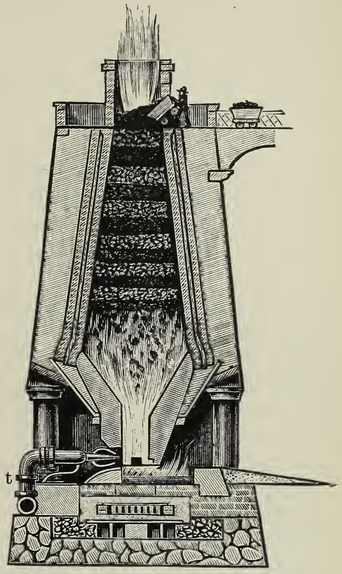


FIG. 92.

We need to consider (1) the nature of the ore. If the ores contain carbonates, they are first roasted to convert them to oxides. This process also serves to expel a portion of the sulphur with which they are frequently contaminated.

(2) The nature of the mineral matters, or *gangue*, with which the ores are associated. It is indispensable that they should be converted into a sort of glass or fusible slag. Hence, if the ores contain clay, they are mixed with lime; or, if they contain an excess of lime, they must be mixed with clay. The most easily fusible slag has nearly the formula, $6\,CaO, Al_2O_3, 9SiO_2$; and it is desirable to obtain this compound as nearly as possible.

(3) Charcoal yields the best iron; anthracite coal, almost as good. The coal should be free from sulphur, and should not cake in the furnace. Caking coals require to be changed to coke before using. Such cokes lose a portion of their sulphur, and become almost, if not quite, as serviceable as the other forms of carbon.

We have now the crude materials, (*a*) the roasted ores, which are oxides of iron; (*b*) the lime or clay, to render the slags fusible (they are called fluxes); (*c*) some form of carbon, which is to act both as a fuel and as a reducing agent; and (*d*) a blast of air to furnish oxygen to the coal.

(4) Now suppose the furnace has been properly heated to avoid cracking the masonry, and a layer of coal is burning at the bottom. Then a suitable mixture of roasted ore and flux is added from the top of the stack, then another layer of coal, then another layer of ore and flux, and so on alternately until the stack is nearly filled up, the heat being maintained by the air blast for some hours.

513. The chemical processes which take place are these:

(1) The air passing through the tuyere pipes combines with the ignited carbon and forms carbonic acid, $C + O_2 = CO_2$. (2) This ascends into the furnace, and, meeting with red-hot carbon, combines with it and forms carbonous oxide, $C + CO_2 = 2CO$. (3) The carbonous oxide, acting upon the iron oxide, reduces it to the metallic state, $Fe_2O_3 + 3CO = Fe_2 + 3CO_2$. (4) At the same time, the heat produced renders the slag fusible, and the reduced iron is disseminated through it until it can gradually sink down to the hottest part of the furnace. (5) There it combines with a small portion of the carbon, forming cast iron (Fe_4C?), a fusible compound which settles to the crucible at the bottom of the furnace. (6) The slag accumulates in larger quantities than the cast iron, and is drawn off, from time to time, through apertures provided for that purpose. (7) Finally, when the cast iron has accumulated in sufficient quantities, it is run through channels into moulds of sand; and, upon cooling, forms rough, cylindrical masses, which are the pig iron, or cast iron, of commerce.

It ought also to be noted that the process is continuous. As fast as the slag and the iron are drawn off at the bottom, fresh materials are added at the top, and the process goes on without stopping for years.

514. Cast iron has many varieties. The extremes are *white* and *gray* iron. White iron is a hard, brittle compound of iron and carbon, nearly represented by the formula Fe_4C (it generally contains about 3 per cent C). It is not suitable for castings, because, although more fusible than gray iron, it is less liquid when fused, and fails to fill the moulds completely. It dissolves completely in hydrochloric acid, yielding hydrogen associated with an unpleasant odor of some hydro-carbon compound. On the

other hand, when gray iron dissolves in hydrochloric acid, it leaves a residue of graphitic carbon.

515. Gray iron, therefore, contains most of its carbon in an uncombined state, as graphite. It is so soft that it may be easily turned in a lathe, and is admirably fitted for castings. An intermediate variety, called mottled cast iron, exceeds both the other varieties in tenacity, and is used for cannon. In commerce there are eight grades distinguished.

The foundry man can control his product to a great extent, although he may obtain pigs of different grades at the same casting. Too small a proportion of fuel—*i. e.*, too low a heat—will yield white iron.

516. Spiegel-eisen is a crystalline variety of white cast iron, containing from 3 to 12 per cent of manganese, and a large amount of combined carbon. It is excessively hard and lustrous, and is chiefly used in the Bessemer process for making steel.

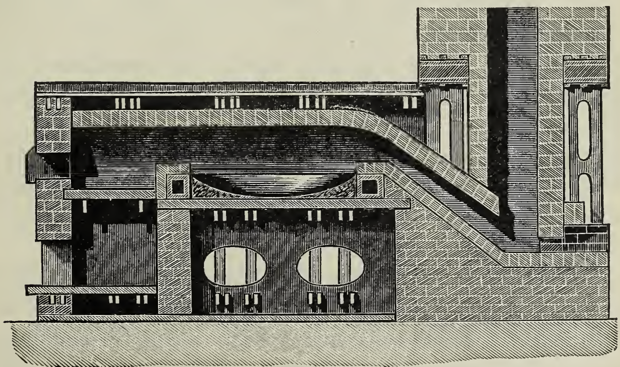


FIG. 93.

517. Wrought, or bar, iron is nearly pure. To obtain it from cast iron, the carbon is burned away. This is effected in a puddling furnace (Fig. 93), which is a reverberatory furnace divided into two parts.

In one side the fuel is placed, and the flame is conducted so as to play on the hearth of the other side. Upon this hearth a mixture of iron oxide and white iron is placed. It soon melts and becomes oxidized upon the surface. The mass is now thoroughly stirred (puddled), whereby the carbon is oxidized and escapes as carbonic oxide. As wrought iron is less fusible than cast iron, the mass becomes more and more pasty, until, when the greater part of the carbon has been driven off, it assumes a pasty condition, or "comes to nature," and collects in a spongy mass upon the end of the puddle. It is then taken from the furnace and beaten or squeezed to free it from silicious slags, and becomes welded into an ingot, or bloom, of wrought iron. These ingots are reheated and rolled into bars, to give the metal a homogeneous and fibrous structure.

It is to this fibrous structure that the tenacity of wrought iron is due. Cast iron, when broken, shows a granular structure, and breaks much more easily than wrought iron. It is said that wrought iron loses its fibrous structure and becomes granular by repeated concussions.

518. Wrought iron is never quite pure. The best contains a minute proportion of carbon (from 0.1 to 0.3 per cent); but this can hardly be considered as a disadvantage, because it notably increases the hardness and tenacity of the iron.

Some varieties of bar iron are brittle when cold. This defect is probably due to the presence of phosphorus, and, perhaps, also of silicon. This is called "cold-shortness."

The presence of sulphur, on the other hand, renders the iron brittle when hot. This defect is called "red-shortness." Iron containing both sulphur and phosphorus has both defects, and is difficult to weld when hot, and is brittle when cold.

519. Steel is a product intermediate between cast and wrought iron. It can be cast like pig iron, and worked on the anvil and welded like wrought iron. Moreover,

it possesses the invaluable property of receiving a "temper." Soft steel, if suddenly cooled from a high temperature, becomes excessively hard and brittle. By subsequent heating it may be rendered as soft and tenacious as is required. This process is called "drawing the temper."

520. Steel contains from 0.5 to 1.5 per cent of carbon. This carbon may be added to wrought iron by heating it for several days at about 1100° C., or below the fusing point of steel, in chests packed with charcoal powder. The product is known as blistered steel, but it is far from being uniform in its composition. When blistered steel is melted and cast into ingots, it becomes homogeneous in structure and is called *cast steel.*

521. The Bessemer process converts cast iron into steel by burning away a portion of its carbon.

This is effected by running several tons of melted cast iron into a large crucible, or converter, provided with tuyeres through which a strong blast of air can be blown. Considerable heat is developed by this operation; nearly all of the carbon is burned away, and the iron becomes nearly bar iron. The moment when this result is accomplished may be determined by the spectroscope, or with sufficient accuracy by the practiced eye of the foreman. Then the blast of air is stopped, and a quantity of melted spiegel-eisen, sufficient to furnish the necessary carbon, is added, and the mixture is allowed to rest for a few minutes, to permit all gases to escape, and then it is cast into ingot moulds.

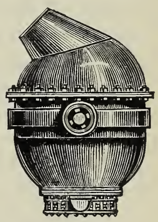


FIG. 94.

This steel is of inferior quality to cast steel, but is admirably adapted for the rails used in railroads, and for other purposes. The presence of $\frac{1}{5000}$ of its weight of phosphorus renders steel brittle.

522. The malleable iron, so-called, which is daily growing into use, is simply cast iron which has been

heated for days in boxes packed with the sesquioxide of iron. The cast iron thereby loses enough of its carbon to become assimilated to wrought iron. When the process is well conducted, small objects of brittle white cast iron, as buckles, gate hinges, or even larger articles, become nearly as malleable and tenacious as wrought iron; and small bars so treated may even be drawn into the finest wire. We observe that this is the reverse of the process of making blistered steel. (1) In steel, the carbon is added by heating wrought iron with charcoal; (2) in malleable iron, the carbon is withdrawn by heating cast iron with ferric oxide.

523. Pure iron is readily prepared by heating its oxide in a current of hydrogen or of carbonous oxide. (§ **295**).

In this connection, **Exp. 30** is very interesting.

Exp. 195.—The apparatus necessary will be readily understood from the figure. (Use apparatus in Fig. 27). The hydrogen is carefully dried by sulphuric acid, and allowed to escape until no air remains in the apparatus. The bulb tube, which contains a small quantity of the pulverized oxide, is then heated to redness and becomes reduced: $Fe_2O_3 + 6H = 2Fe + 3H_2O$; or, if carbonous oxide be employed, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. The reduced iron must be allowed to cool in a current of the gas before the iron is poured out.

524. Iron so reduced is a black powder. It so readily oxidizes that it may be set on fire by a lighted splinter; or, if poured from the reduction tube while warm, takes fire in the air and again changes to the oxide. Pure iron in its compact form is a silvery-white, strongly magnetic metal, exceedingly ductile, malleable, and tenacious, but soft enough to permit its being easily cut with steel files. It fuses at white heat; but, fortunately for the arts, before reaching this temperature it becomes so soft that it may be wrought on the anvil and welded. The blacksmith usually sprinkles sand or borax on the heated metal, in order to form with the oxide film a

fusible slag, which may be forced out by the hammer, and thus leave the surfaces clean. They then cohere or weld without difficulty.

525. Iron does not oxidize in dry air at ordinary temperatures. (1) When heated in air, a blackish "scale oxide" forms, which is beaten off by hammering. (2) In moist air, it rapidly oxidizes, or "rusts." The water decomposes, and ferrous oxide forms: this in the presence of carbonic anhydride becomes ferrous carbonate; and this, in turn, becomes ferric hydrate ($Fe_2O_3, 3H_2O$). Unfortunately, this is very porous; and these changes, when once commenced, go on with increasing rapidity until the entire mass is corroded. (3) Heated in a current of steam, iron decomposes water readily; thus, $3Fe + 4H_2O = Fe_3O_4 + 8H$.

Dilute hydrochloric and sulphuric acid dissolve iron readily with evolution of hydrogen, and form respectively ferrous chloride and ferrous sulphate. Dilute nitric acid also dissolves it, evolving nitric oxide and forming, when the action is rapid, ferric nitrate. In strong nitric acid (sp. gr. 1.45) the iron assumes a "passive condition," in which it is neither attacked by the strong acid nor afterward by nitric acid of ordinary strength (sp. gr. 1.35).

526. The uses of iron are so varied and well known that it is useless to attempt to enumerate them. The alloys are not of much importance. When protected from the action of the air by a coating of tin, it forms the tin plate of commerce; and when coated with zinc, it is called galvanized iron.

527. The compounds of iron. Although the two series of iron salts differ widely, they are easily converted from one form to the other. Solutions of ferrous salts quickly oxidize in the air, and soon manifest the presence of ferric salts. They are more quickly oxidized by

nitric acid or by a mixture of potassium chlorate and either hydrochloric or nitric acid. On the other hand, reducing agents like nascent hydrogen, sulphuretted hydrogen, stannous chloride, and sulphurous anhydride, convert ferric salts to ferrous.

528. **Ferrous salts,** when crystallized, have generally a green color and astringent taste. Such as are soluble can be easily made by dissolving iron in the cold dilute acid required.

Ferrous sulphate, $FeSO_4 + 7H_2O$ (*copperas* or *green vitriol*), may be obtained pure from the mixture of iron sulphide and sulphuric acid used in making sulphuretted hydrogen: $FeS + H_2SO_4 = H_2S + FeSO_4$. The remaining solution requires merely to be filtered and crystallized out, preferably under a layer of alcohol. Exposed to the air, the crystals absorb oxygen and form a basic ferric sulphate. Hence, ferrous sulphate may act as a reducing agent, as already noted in gold. It is largely used as a disinfectant, and for making "white indigo."

Ordinary black ink is made from a solution of nut-galls and a sulphate of iron. If ferric sulphate is used, the ink is black when first applied; if ferrous sulphate is used, the ink is first a pale green, but becomes black on exposure to the air.

Ferric sulphate, $Fe_2(SO_4)_3$, is a yellowish, difficultly soluble body, obtained by oxidizing the ferrous sulphate. The basic sulphate is used in making Nordhausen acid.

529. **On heating iron wire** in a stream of dry chlorine gas, a volatile anhydrous chloride is formed, which collects in the cooler parts of the tube. (1) When the iron is heated to redness, white or yellowish shining scales of ferrous chloride form; (2) at a lower heat, and especially in the presence of air, iridescent spangles of ferric chloride form.

Hydrated ferrous chloride is formed when iron wire is dissolved in hydrochloric acid, and the mixture left

to cool in closed vessels. This is changed to ferric chloride by the addition of nitric acid until the solution becomes a yellowish brown. It forms, when dried, a yellow, deliquescent mass. It is also to be noted that both chlorides volatilize even from their solutions when heated.

530. Ferrous carbonate, $FeCO_3$, is probably formed when sodium carbonate is added to a solution of ferrous sulphate; but it soon loses its carbonic anhydride, oxidizes, and yields ferric oxide. It is soluble in an excess of carbonic anhydride, and is found dissolved in mineral waters. It also exists in most blue clays. When these mineral waters are exposed to the air, the ferric hydrate precipitates, sometimes forming an iridescent, oily looking film on the water; and, when such clays are burned, they impart a red color to the bricks, tiles, etc.

531. Iron exhibits strong affinities for sulphur. Ferric sulphide, FeS_2, occurs abundantly in nature as iron pyrites, in yellow, hard crystals strongly resembling gold (fool's gold), but easily distinguished from it by its lower density and superior hardness, and by its giving off sulphurous anhydride when strongly heated in air. This last reaction renders it an available means for the preparation of sulphuric acid.

When a mixture of iron filings and sulphur ($\frac{56}{88}$ Fe, $\frac{32}{88}$ S) are heated together, they combine and form a grayish-black mass of ferrous sulphide, FeS, which is invaluable for the preparation of sulphuretted hydrogen. There are many other sulphides, corresponding to the various oxides.

532. The consideration of the oxides of iron has been reserved to this point, because in them we have valuable tests of iron.

(1) A solution of a ferrous salt, when mixed with a solution of sodium hydrate, yields a white precipitate

of ferrous hydrate, $Fe(OH)_2$, which readily oxidizes in the air—becoming green, then black, and finally reddish brown.

(2) The reddish brown result is ferric hydrate, $Fe_2(OH)_6$. It is obtained directly as a voluminous precipitate by adding sodium hydrate to a solution of a ferric salt. After ignition, it shrinks in volume and is changed to Fe_2O_3. Ammonia produces the same precipitate in ferric salts; but forms with ferrous compounds soluble double salts.

(3) When iron is burned in air, a black compound forms which is principally Fe_3O_4, "scale oxide." This form occurs also in nature, and some specimens of it are natural magnets.

(4) When iron and saltpeter are fused together, and then treated with water, a purple solution is obtained, which is supposed to contain K_2O, FeO_3, potassium ferrate. Ferric anhydride, FeO_3, has never been isolated.

Special Tests for Iron.

(1) When sulphuretted hydrogen is passed through acid solutions of ferric salts, they are reduced, with separation of sulphur, but no further change is produced.

(2) Alkaline sulphides precipitate both ferric and ferrous salts as ferrous sulphide, FeS, a black pulverulent precipitate.

(3) Ammonium sulphocyanide, $(NH_4)CyS$, changes solutions of ferric salts to a beautiful blood-red color, even when the iron is present in very small quantities.

(4) Distinctive reactions are produced when solutions of ferro- and ferri-cyanide of potassium are added to solutions of iron, very slightly acidulated.

	WITH FERROUS SALTS.	WITH FERRIC SALTS.
Ferrocyanide, $K_4(FeCy_6)$	Everitt's White, $K_2Fe''(FeCy_6)$	Prussian Blue, $(Fe^{IV}{}_2)_2(FeCy_6)_3$.
Ferricyanide, $K_3(FeCy_6)$	Turnbull's Blue, $Fe''_3(FeCy_6)_2$	No precipitate; solution becomes brown.

Manganese.

533. Manganese is related not only to zinc, to iron, and to chromium, but probably also to chlorine. It generally occurs in nature as an oxide, MnO_2, Mn_2O_3, or as "*wad*," which is a mixture of these with earthy matters.

The metal is seldom prepared, but may be obtained from its oxide by reducing with carbon at white heat. It is very hard and brittle, slightly magnetic, easily oxidized in moist air, and capable of decomposing hot water.

534. It forms four series of compounds. (1) As a dyad element, salts like $MnCl_2$ or $MnSO_4$, obtained by heating its oxides with hydrochloric or sulphuric acid; as, $MnO_2 + 4HCl = 2H_2O + MnCl_2 + \widehat{Cl_2}$ or $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + \widehat{O}$. These salts are pinkish colored, and crystallize in forms isomorphous with zinc salts, as $MnSO_4 + 7H_2O$. They are the usual compounds in which manganese acts as a positive element. Their solutions, when treated with sodium hydrate, yield a white precipitate of hydrated manganous oxide, which rapidly oxidizes in the air, and finally becomes brown $Mn_2O_3, 3H_2O$. When ammonium sulphide is added to solutions of these salts, it forms flesh-red manganous sulphide, MnS, a characteristic test, not only by reason of its color, but also because it is the only sulphide of the group which is soluble in acetic acid.

(2) As a tetrad element, in oxides like MnO_2 (*pyrolusite*), or with a double atom like Mn_2O_3 (*Braunite*). These, when heated with hydrochloric acid, yield free chlorine and form manganous chloride.

There is, besides, an unstable green sulphate of this group, which forms a moderately stable alum with alkaline sulphates, as $K_2O, SO_3 + Mn_2O_3, 3SO_3 + 24H_2O$.

(3) As a hexad element, neither MnO_3 nor $MnCl_6$ are known; but, when any oxide of manganese is fused with saltpeter, a deep-green, easily soluble mass is obtained, which is potassium manganate, K_2O, MnO_3 or K_2MnO_4. This body is so unstable that it is easily decomposed by water or by acetic acid, forming a rose-red solution of the permanganate.

(4) The potassium permanganate has the formula K_2O, Mn_2O_7 or $KMnO_4$. As this salt is isomorphous with the potassium perchlorate $KClO_4$, it is supposed that manganese acts in this as a septad element like chlorine.

535. Potassium permanganate crystallizes in beautiful red rhombic prisms, freely soluble in water. It is more stable than the manganate, but both are strong oxidizing agents, readily giving up most of their oxygen and reverting to manganous oxides, especially in the presence of free acids. Hence, the potassium permanganate is much used in volumetric analysis.

Exp. 196.—Acidulate a solution of a ferrous salt, and add drop by drop, a solution of a permanganate. The red color of the permanganate solution does not remain permanent until all the ferrous salt has been oxidized to ferric:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Hence, if the quantity of the permanganate used is known, that of the ferrous oxide present can be calculated.

From the readiness with which both the manganate and permanganate salts are decomposed, they are used as disinfecting agents. They are especially useful in detecting the presence of decomposing organic bodies in waters used for drinking.

536. The uses of manganese are chiefly (1) in the preparation of the disinfecting agents already mentioned; (2) in making glass, to which it imparts an

amethyst color when alone, or, when mixed in the required amount, destroys the green color produced by iron; (3) in the preparation of chlorine used in the manufacture of bleaching powder.

TESTS.—Some of the tests for manganese have already been indicated. The most characteristic are the flesh-red sulphide and the potassium manganate formed by fusion with niter.

In its other reactions it agrees generally with the members of this group, except that its white hydrate in alkaline solutions is more readily oxidized by air or by chlorine to the brown sesquioxide, Mn_2O_3.

CHROMIUM AND ALUMINIUM.

537. **These elements** are closely related to iron. Chromium is considered first, because it forms a series of dyad compounds represented by $CrCl_2$ and the double sulphate, $K_2O, CrO, (SO_3)_2 + 6H_2O$. These chromous compounds are generally unstable; and chromous chloride is so readily changed to its higher compounds that it is one of the most powerful reducing agents known. They are also seldom met with, and will not be considered further. It also forms an unimportant oxide, Cr_3O_4, resembling magnetite.

538. **In the tetrad series,** both of these elements, Al_2O_3 and Cr_2O_3, form salts which strongly resemble ferric salts, and are isomorphous with them. The only oxide of aluminium is Al_2O_3, which acts both as a weak base and as a weak acid.

Chromium forms also a hexad series, like iron and manganese. In this series it acts as a negative element, as K_2O, CrO_3

539. **The most important ore of chromium** is chrome iron, $FeCr_2O_4$, or, perhaps, FeO, Cr_2O_3. It also occurs in a few other minerals as red lead ore, $PbCrO_4$, and is the green coloring principle of the emerald.

Metallic chromium has no use in the arts, and is seldom prepared. It is one of the most infusible of metals, and so hard as to scratch glass. Combined with steel, it forms an exceedingly hard alloy, which has found employment in cutting glass, sharpening knives, and in making drills.

540. The compounds of chromium. Unlike the metals previously studied, chromium ores are worked only for the sake of their salts. The first formed are the chromates; the other salts are derived from them by subsequent treatment.

The pulverized chrome iron ore is mixed with potassium carbonate and potassium nitrate, and is then heated in a current of air on the hearth of a reverberatory furnace. The Cr_2O_3 is oxidized to $2CrO_3$, and unites with the potassium to form potassium chromate.

541. Potassium chromate, K_2O, CrO_3. This salt is obtained by lixiviating the ignited mixture and evaporating the solution. It forms very soluble, yellow, rhombic crystals.

542. Potassium bichromate, $K_2O, 2CrO_3$ or $K_2Cr_2O_7$, is the usual salt found in commerce. It is prepared by mixing the solution of the chromate with nitric acid: $2(K_2O, CrO_3) + H_2O, N_2O_5 = H_2O + K_2O, N_2O_5 + K_2O, 2CrO_3$. The salt is soluble in 10 parts of water, and crystallizes in beautiful red, tabular prisms. With an excess of nitric acid, a red ter-chromate is also formed, $K_2O, 3CrO_3$.

543. Chromic anhydride, CrO_3, is obtained by mixing a saturated solution of the bi-chromate with a little more than its own bulk of sulphuric acid. When this mixture cools, the chromic anhydride separates out in crimson needles. These crystals are deliquescent, and are very soluble in water. Although a moderately stable

body, it is a powerful oxidizing agent, and is instantly reduced by organic matters and by all reducing agents, as H_2S, SO_2, Zn, and even by HCl. Hence, its solution can not be filtered through paper, and the crystals formed as above described must be separated from the mother liquor by decantation, and dried upon a porous tile.

Exp. 197.—Place upon a saucer dry chromic anhydride, and pour upon this a little alcohol. The CrO_3 is reduced partly to Cr_2O_3 and partly to CrO_2; the alcohol is changed to *aldehyde:* $3(C_2H_6O)$ alcohol $+ 2CrO_3 = 3H_2O + Cr_2O_3 + 3(C_2H_4O)$ aldehyde. So much heat is evolved that the alcohol is frequently set on fire.

544. Chromic acid, H_2O, CrO_3 or H_2CrO_4, has never been isolated; but there is a large number of chromates which are generally yellow or red salts. Many of these are used as pigments, and are easily obtained by mixing a solution of potassium bi-chromate with a solution of a salt of some other metal.

(1) With lead acetate, $PbCrO_4$ forms as a beautiful yellow precipitate, which is "chrome yellow." "Chrome green" is a mixture of this with Prussian blue.

(2) With barium chloride it forms a pale yellow precipitate of $BaCrO_4$, which is "yellow ultramarine."

(3) With silver nitrate and with mercurous nitrate, the products are red chromates, which are beautiful colors, but too expensive to be used as pigments.

There are numerous other chromates, most of which, except those of the alkalies and of strontium, calcium, and magnesium, are insoluble in water. They are all decomposed by heat, with evolution of oxygen.

545. Lead chromate is used as an oxidizing agent in organic analysis. When heated with sulphuric acid, the chromates are reduced with evolution of oxygen—*e. g.*, $2CrO_3 + 3H_2SO_4 = Cr_2O_33SO_3 + 3H_2O + 3\widehat{O}$; and by hydrochloric acid, with evolution of chlorine:

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 6\widehat{Cl}.$$

These last reactions will take place when a chromate is heated with these acids, and an excess of acid must be used in order to combine with the base of the chromate.

546. There are also several compounds of this series, of great theoretical interest. One of these is CrO_2Cl_2, in which two chlorine atoms have displaced one atom of oxygen. It is obtained by distilling a mixture of common salt and sulphuric acid with potassium bichromate, as a blood-red liquid, which is a powerful oxidizing agent, commonly called *chlorochromic anhydride.* At the same time, there forms a salt which is $K_2Cr_2O_6Cl_2$, or a potassium bi-chromate in which one atom of oxygen is replaced by two atoms of chlorine.

547. Chromium acts as a negative element in this series. It also acts as a positive element in a totally different series. *Chromic oxide,* Cr_2O_3, is obtainable as an amorphous green powder by igniting chromic anhydride, or by igniting any chromate containing a volatile base, as NH_4 or Hg. It is used as a green pigment, and is especially valuable for imparting a beautiful green color to glass and porcelain. This oxide is almost insoluble in acids.

548. The other compounds of this series are most easily prepared from chrome alum. Chrome alum is itself made (1) by heating a mixture of potassium bichromate and sulphuric acid with alcohol; or (2), better, by passing through the mixture, in the cold, a stream of sulphurous anhydride: thus, $K_2O,2CrO_3+H_2SO_4+3SO_2=H_2O+(K_2O,SO_3+Cr_2O_3,3SO_3)$. On crystallizing, splendid dark purple octahedra form, which contain $24H_2O$, or are $KCr(SO_4)_2+12H_2O$.

549. Chromic hydrate, $Cr_2O_3,3H_2O$, may be precipitated from a solution of chrome alum by any alkaline hydrate. It is a bulky, greenish-blue powder, soluble in excess of soda or potash, but is again precipitated

on boiling. It is a feeble base, but is remarkable for forming with the acids two classes of salts, which are identical in formulæ, but differ in some of their properties. (1) Violet salts formed (when a rise in temperature is avoided) by dissolving the hydrate in acids. These salts are crystallizable, and are insoluble in alcohol. (2) Green salts, which are obtained on boiling the violet salts. They are uncrystallizable, but are soluble in alcohol. The green salts, when kept in solution for months, gradually recover their violet color and become crystallizable. These are marked examples of isomerism among inorganic compounds.

550. Chromic sulphate, $Cr_2(SO_4)^3 + 18H_2O$, is obtained by dissolving chromic hydrate in dilute sulphuric acid. If prepared in the cold, it has a violet color; but, when heated, becomes green, reverting after a time in solution to the violet modification.

551. Chromic chloride, $Cr_2Cl_6 + 12H_2O$, forms when chromic hydrate, or any chromate, is dissolved in hydrochloric acid. An anhydrous chloride of a beautiful peach-blossom color, which is scarcely soluble in boiling water or in acids, is formed when chlorine gas is passed over ignited chromic oxide.

It is also supposed that there is a perchromic acid, H_2O, Cr_2O_7, which is formed when peroxide of hydrogen is added to chromic salts. A blue solution is thereby formed, which is a delicate test for chromium; but neither the acid nor its salts have been obtained.

552. Uses of chromium. The chromates are valuable oxidizing agents, especially in the presence of sulphuric acid. Potassium bichromate solution is frequently used in galvanic batteries. Principally, however, chromium compounds are used in dyes and pigments. They are generally yellow or green. The green printing ink used in "green-backs" owes its color to chromium.

TESTS FOR CHROMIUM.—(1) All chromium compounds, when heated with borax, yield an emerald-colored bead which is very characteristic.

(2) All chromium compounds, when fused with soda and niter, yield a yellow chromate soluble in water.

(3) These chromates, neutralized with acetic acid, yield characteristic precipitates: yellow with lead and barium; red with silver and mercurous salts.

(4) The chromates in solution are reduced to salts of the sesqui-oxide by sulphuretted hydrogen. These reduced solutions, or solutions of salts of the sesqui-oxide, yield, with ammonium sulphide or ammonia, greenish or bluish hydrates, somewhat soluble in excess of the precipitant, but again precipitated upon boiling.

ALUMINIUM.

553. Aluminium is one of the most abundant and most widely distributed of the elements. It never occurs native, and seldom occurs as an oxide (emery, corundum), but more frequently as a fluoride (cryolite). It forms, however, an almost endless variety of double silicates, which constitute the great majority of the rocks of the earth, as granite, basalt, slates, shales, and clays. The feldspars and micas are silicates of alumina combined with silicates of potash, or soda, or lime, or magnesia, or a mixture of these with small amounts of other bases. When such minerals as these disintegrate by the action of atmospheric agencies, ordinary clays, potter's clay, fire clay, and kaolin are formed, which are aluminic silicates, more or less contaminated with other substances. Alumina is also a constituent of several precious stones, as the sapphire, ruby, topaz, emerald, and garnet.

554. Aluminium is best prepared by fusing the double chloride of aluminium and sodium with metallic sodium: $2NaAlCl_4 + 6Na = 8NaCl + 2Al$. The addition of cryolite ($Al_2Na_6F_{12}$) facilitates the reduction. It is a bluish-white metal, of very low specific gravity (2.56), which

is quite malleable, ductile, and tenacious. It is also remarkably sonorous, which property it also communicates to many of its alloys. Aluminium is not oxidized in the air nor affected by sulphuretted hydrogen. It is not attacked by cold dilute sulphuric and nitric acids, but dissolves readily in hydrochloric acid and in solutions of caustic soda and potassa.

Its many valuable properties render it desirable that it should be more abundantly used in the arts and in the various appliances of the household; but the cost of its preparation (which is dependent on the price of sodium) has restricted its application mainly to the construction of delicate balances, small weights, and other instruments in which lightness is desired and only a moderate strength needed.

Much has been hoped for the alloys of aluminium. Aluminium bronze contains 9 parts of copper and 1 part of aluminium. It is very strong, difficultly fusible, unaltered in air, but has not found a wide application in the arts.

555. The compounds of aluminium. As already stated, aluminium forms but one series of compounds, the tetrad, represented by Al_2O_3 and by Al_2Cl_6.

Alum is the most important salt. The simplest process by which it is manufactured consists (1) in forming aluminium sulphate by heating a pure clay or shale with sulphuric acid. On lixiviating this mass, an aluminium sulphate is obtained: $Al_2O_3, 3SO_3 + 18H_2O$. (2) Because this salt is difficultly crystallizable, it is converted into a double salt containing either K_2O, SO_3 or $(NH_4)_2O, SO_3$, which crystallizes in beautiful octahedra, in a condition which insures the purity of the commercial article. This is effected simply by mixing the solution of aluminium sulphate with the requisite amount either of potassium or of ammonium sulphate, and allowing the solution to crystallize. The crystals have the formula $K_2O, Al_2O_3, 4SO_3 + 24H_2O$ and

$(NH_4)_2O, Al_2O_3, 4SO_3 + 24H_2O$; or, written in molecular formulæ,

$$KAl(SO_4)_2 + 12H_2O \text{ and } NH_4Al(SO_4)_2 + 12H_2O.$$

Formerly, potassium alum was the most common; but now the ammonium alum has become the usual commercial article, because the ammonium sulphate is obtained at a low price from the refuse liquors of gas works. The value of either alum depends only on the amount of aluminium sulphate it contains.* Of late years, aluminium sulphate has found its way into commerce under the name of concentrated alum.

556. Aluminium hydrate, $Al(OH)_3$, is formed as a white gelatinous precipitate when ammonia or (avoiding excess) any other alkali or alkaline carbonate is added to a solution of alum. With a small amount of alkaline carbonate, a basic sulphate, Al_2O_3, SO_3, is formed. The use of alum in the arts depends upon the fact that both the hydrate and the basic salt have the power of combining with the coloring principles of organic dyes, like cochineal, to form insoluble pigments called lakes, as carmine.

In applying this reaction to calico printing, (1) the stuffs are dipped in a solution containing this basic alum, when the cloth becomes impregnated with the aluminium compound. (2) By the action of air or of steam, the aluminium becomes firmly incorporated with the fibers of the cloth. This is the "ageing process." (3) The cloth is now dipped into the dye-vat, and the aluminium combines with the coloring matters and fixes them within the fiber. Such colors are likely to be "fast," that is, durable; and the alumina is said to act as a "mordant," because it bites or holds the colors.

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* The word alum, which was once used specifically to denote potash alum, is now generically applied to all double sulphates which crystallize in octahedra with $24H_2O$, and contain a monad sulphate together with a tetrad sulphate; thus, $R'_2O, SO_3 + R^{IV}_2O_3, 3SO_3 + 24H_2O$. In this way we may have a large series of iron, chromium, and aluminium alums with either of the alkalies, potassium, sodium, etc. There are also a number of pseudo-alums with $22H_2O$, containing dyad metals like magnesium.

Aluminium hydrate is easily soluble in dilute acids, forming salts such as $Al(NO_3)_3$; Al_2Cl_6. The chloride forms a number of double salts with the alkaline chlorides.

557. Aluminium oxide, Al_2O_3, or *alumina*, occurs in nature nearly pure in corundum, and in an impure state as emery. Both of these are extremely hard, and are used for polishing. It is artificially obtained as a white amorphous powder by igniting aluminium hydrate or ammonia alum. It is then an almost infusible mass, and is insoluble in acids. It is rendered soluble by fusion with carbonates of soda or of potash. The compounds thus formed are aluminiates, in which the aluminium acts as a negative element.

558. Potassium aluminiate, K_2O, Al_2O_3 or $KAlO_2$, is crystallizable; *sodium aluminate* is a white amorphous solid. Solutions of either of these are decomposed by acids, even by carbonic, forming aluminium hydrate. Hence, they may be used as substitutes for alum.

The affinities of aluminium in both these classes of salts are very feeble; for, if a solution of an aluminium salt is mixed in atomic proportions with one of an aluminiate, both are decomposed with the formation of aluminium hydrate; for example:

$$Al_2Cl_6 + 6KAlO_2 + 12H_2O = 4Al_2O_3, 3H_2O + 6KCl.$$

559. Ultramarine, a beautiful blue pigment, was formerly obtained from *lapis lazuli*, one of the precious minerals. After careful analyses of the mineral, attempts were made to reproduce the pigment artifically, by fusing together the materials in the proportions so ascertained. Finally, it was found that by fusing together pure clay, sodium sulphate, and charcoal, a green "ultramarine" was produced which is a valuable pigment. This product, mixed with sulphur and again fused, yields a blue ultramarine which fairly rivals in brilliancy of color the native mineral, and is much cheaper.

This may be considered as one of the triumphs of chemistry; although, even now, the cause of the beautiful blue color in either the native or artificial ultramarine has not been satisfactorily ascertained. We know only that they contain sodium-aluminium silicates and sodium polysulphide as their principal ingredients.

560. Aluminium silicates are of great importance. They are seldom found pure in nature, being generally contaminated with iron and other bases. The purest is kaolin, a white friable clay derived from the decomposition of feldspars. These clays are used in the manufacture of porcelain; the more impure clays, in the manufacture of bricks.

Limestones containing about 20 per cent of aluminium silicate when calcined yield hydraulic cements, which have the property of hardening under water.

TESTS.—(1) Solutions of aluminium salts are precipitated as white gelatinous hydrates, $Al(OH)_3$, by ammonium hydrate and ammonium sulphide, almost completely.

(2) The hydrate, when moistened with cobalt nitrate, and ignited, forms an infusible blue mass.

Gallium, discovered by Lecoq de Boisbaudran in 1876, is probably related to aluminium. It has been obtained in whitish octahedral crystals (sp. gr. 5.9), which, though harder than iron, melt at a temperature of about 30°C. Its atomic weight has recently been determined 69.9.

Recapitulation.

The elements in this group form compounds in which they enter as dyads, tetrads, and hexads.

The dyad compounds strongly resemble those of Mg, Zn, and Cd, being isomorphous with them, and capable of replacing them in the double salts with the alkalies, as in $R'_2O, SO_3 + R''O, SO_3 + 6H_2O$. All these dyad compounds are precipitated by

sodium hydrate, avoiding excess, as white or greenish hydrates, soluble in a large excess of ammonium chloride. H_2S does not precipitate Mg; it precipitates CdS in acid and alkaline solutions, and the others only in alkaline solutions or by alkaline sulphides, as sulphides. Their protoxides are generally strong bases.

The hydrates of the tetrad series are weak bases of the formula $R^{IV}_2O_3, 3H_2O$. They are precipitated on adding to their neutral solutions almost any dyad carbonate. The best reagent is $BaCO_3$. They do not dissolve in ammonium chloride, and hence are also precipitated by NH_4HO. These hydrates also in some cases act as weak acids. Their sulphates form with alkaline sulphates double salts containing $24H_2O$ (alums). Cr and Al do not form sulphides in the wet way.

Some of these elements form also a hexad series, in which they act as negative elements. The best representatives of this class of compounds are the salts of the acids of manganese and chromium, as K_2MnO_4, K_2CrO_4.

These three series differ widely from each other. Al forms only tetrad compounds. The dyad compounds of the others are changed by oxidizing agents to tetrad compounds; some (not all) of the tetrads may be further oxidized by fusion with niter to hexad compounds. On the other hand, reducing agents will convert hexads to tetrads, and most tetrads to dyads. These elements therefore exhibit a very flexible character.

It is not improbable that Mn and Cr also act as heptads in $KMnO_4$ and in perchromic acid.

The metals of this group have important uses in the arts; iron being, perhaps, the most used and the most useful metal known. Many of their alloys and salts find important applications in the arts. Fe, Co, Ni, and Mn are magnetic elements.

It may also be noted that while these elements agree in some particulars, they differ in many others. Some form by preference dyad compounds; Al only tetrad; Cr is best known as a hexad. Nevertheless, the pairs which make up the sub-groups are strongly related.

CHAPTER XVI.

KERAMICS AND GLASS.

561. Bricks are made from clay. This is kneaded with a small amount of water, so as to render the mass homogeneous; then moulded into shape; then thoroughly dried in the open air; and, finally, burned.

Not all varieties of clay are suitable for this purpose. All clays shrink on drying; but the very plastic clays, which are composed for the greater part of aluminium silicate, shrink so much that they crack and fall into pieces. Hence, an admixture of sand is necessary, which must be supplied, if not naturally present in the clay, in order to give the right consistence to the mass. In tropical countries, the bricks are not burned, but are only sun-dried. These are at best very friable, and are suitable only for low structures.

A small quantity of lime or of feldspar is also a useful constituent of the clay; for, when the bricks are burned, these substances fuse and serve to cement the particles of the clay together. An excess of lime renders the bricks too brittle.

When the clays contain no ferrous carbonate, the bricks, when burned, have a yellow color. The red color of ordinary bricks is due to the conversion of the ferrous carbonate to the ferric oxide, by the action of the heat and the atmospheric oxygen.

Fire-bricks are made from clays which contain neither lime nor iron. These clays fuse less easily than the impure varieties, but they are also capable of resisting the action of fire, and are therefore employed for the lining of furnaces and for crucibles.

All bricks are porous, excepting the few that are burned in immediate contact with the fire. These become so over-heated that their materials fuse and form a sort of glaze over their surface.

The so-called terra-cotta wares are made in the same manner, except that a greater care is taken in moulding the clay and in burning.

562. **Ordinary pottery** is made from the better qualities of clay mixed with sand. Drain pipes and tiles are fashioned by machinery. Most of the hollow vessels are fashioned by hand upon a potter's wheel. The articles are then allowed to dry very slowly. When thoroughly dry, they are baked in kilns. Porous goods, like drain pipes and flower pots, receive no further treatment. Stoneware vessels are glazed in a very simple manner by a process known as salt glazing.

The ware is coated with a thin film of sand by dipping into a mixture of fine sand and water. It is then intensely heated in the kiln, and a quantity of damp salt thrown in. The joint action of the steam and the salt converts the sand into sodium silicate, which fuses to a glass on the surface of the ware.

Other of the cheaper forms of pottery are glazed by dipping the wares into a mixture of clay and litharge. This fuses in the kiln to a lead glass.

563. **Porcelain.** In the manufacture of porcelain, especial care is taken in selecting a nearly pure aluminium silicate: this is kaolin. But it is too infusible a substance to be used alone, and, therefore, requires the addition of some more fusible material, as feldspar. The Vienna porcelain and "china" contain quartz also.

The materials are first ground together, mixed with water, and moulded like ordinary pottery into any required shape, and then are allowed to dry slowly in the air. These dried vessels are then burned in kilns, in which a high temperature may be obtained, and are thereby baked to a white, porous body, which is incorrectly termed biscuit ware. It then requires to be glazed. The best glazing is obtained by dipping the biscuit ware in water containing a mixture which very nearly resembles the original materials, only a little more fusible, and sometimes containing chalk or gypsum. The ware is again reheated to a temperature sufficiently high to fuse the glaze, and is then ready for market.

There are several varieties of porcelain: (1) a very hard sort, like that of China and Japan, which contains a notable amount of quartz; (2) a softer sort, like that of Sevres, which is quite translucent. This translucency is secured by the admixture of "*fritt*" (which consists of a vitrified mixture of sand and alkaline materials) to the kaolin. (3) The English porcelain, which is quite hard but opaque, contains a large proportion of calcined bones.

In the less valuable varieties of porcelain, the glaze frequently contains lead or boracic acid mixed with the silicates. This glazing requires a less temperature for fusing in the second baking; but it is liable to crack, because it is not homogeneous in structure with the body.

564. Glass requires that the materials of which it is composed should be capable of being thoroughly fused together, and, on cooling, yield an amorphous, transparent mass, not easily affected by water or by atmospheric agencies. It is a mixture of various silicates, of which the most common are those of lime, sodium, and potassium.

The cheapest variety of glass (*bottle glass*) is a double silicate of alumina and lime. This mixture is so difficultly fusible that sodium silicate is generally added. The other varieties of glass either contain no alumina or a very small quantity.

Ordinary *window glass* is a mixture which may be very nearly represented by the formula, $Na_2Ca\,4SiO_3$.

The materials used in its preparation are clean white sand, slaked lime, and sodium carbonate; or, instead of the last, a mixture of sodium sulphate with sufficient charcoal to decompose the sulphuric acid. All sodium glasses have a bluish tinge, from which potassium glass is free.

The best *plate glass* is also chiefly a silicate of soda and lime, but also contains potassium silicate.

Crown glass and *Bohemian glass* contain no soda. They

have approximately the formula, $K_4Ca_315SiO_3$. They are beautiful, clear glasses, well adapted for optical purposes. *

Flint glass is a double silicate of potassium and lead prepared by fusing together the purest white sand or flint, calcined and ground, with lead oxide and refined pearl ash. Other materials are also added in small quantities, to prevent the reduction of the lead (KNO_3), or to remove the color which would be produced by the presence of iron (As_2O_3 or MnO_2). Its approximate formula is $K_4Pb_310SiO_3$. The presence of the lead silicate greatly increases the fusibility of the glass, and also adds to its luster and beauty. It is much used for ornamental purposes, as fine cut glass. † In optical instruments, lenses of flint and crown glass are frequently combined to form achromatic lenses. The dispersive powers are made to neutralize each other, and yet leave a considerable index of refraction.

Other silicates are frequently used in glass, as baryta and zinc. Sometimes, also, a quantity of boracic acid is used to replace a portion of the silica.

565. Many metallic oxides impart characteristic colors to glass. Ferrous silicate produces a green glass; ferric silicate, a yellow which is hardly noticeable when in small quantities. Hence, except for green bottle glass, it is desirable to oxidize the iron which is scarcely ever absent from the sand. This is effected by niter, arsenious oxide, or red lead. Manganese binoxide also decolorizes green ferrous silicate; but it is a disputed question whether it effects the change by acting as an oxidizing agent, or by producing a glass of a complementary color, since by itself it yields an amethyst purple glass.

The agents used to impart colors to glass are princi-

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* Index of refraction, 1.53; coefficient of dispersion, 0.02.
† Index of refraction, 1.64; coefficient of dispersion, 0.04.

pally these: red, Cu_2O; ruby, purple of Cassius (Au); amethyst, MnO_2; blue, CoO; green, FeO, Cr_2O_3, CuO; yellow, Sb_2O_3; greenish yellow, U_2O_3. An excess of lead oxide also produces a yellow glass.

566. The manufacture of glass can only be sketched.

The materials are fused together in large pots made of fire-clay, and are then permitted to remain for some time to allow air-bubbles to escape, and to remove the glass scum which rises to the surface. It is then taken from the pots and wrought into the shape required. Much of our glass-ware is blown, as bottles. Tumblers, glass plates, etc., are generally moulded.

All glass-ware, after being shaped, requires to be carefully annealed. This is effected by a process of slow cooling. The hot ware is passed through a long chamber so arranged that the heat is gradually diminished, and the glass is taken from the extreme end quite cool. Unannealed glass is very liable to crack with sudden changes of temperature.

Cut glass receives additional treatment, being ground and afterward polished on emery wheels.

Recapitulation.

Bricks, ordinary pottery, and porcelain require that the materials used (clay, kaolin) should be difficultly fusible.

These materials are kneaded together, dried, and baked. Stoneware and porcelain are then covered with a glaze, and baked a second time.

Glass requires that the materials used should be easily fusible, and furnish a transparent mass.

Glass requires no second baking, but requires a careful annealing.

ORGANIC CHEMISTRY.

CHAPTER XVII.

COMPOUNDS OF CARBON.

567. The compounds of carbon are so numerous and so intimately related to each other that it is convenient to study them after the general principles of Chemistry have been mastered. The laws which govern in their formation and transformations are in no respect different from those of the other elements. This division of the science is frequently termed Organic Chemistry, because many of the carbon compounds have been obtained from plants and animals. Such, for example, are starch, cane sugar, albumin, and glue. Other "organic" compounds have been obtained from these by the natural processes of decay and fermentation, as the grape-sugar, alcohol, and acetic acid that are so derived from starch.

568. In 1828, Woehler obtained urea from ammonium isocyanate. Now, as the cyanogen compounds may be obtained from potassium cyanide, KCN, and this by direct union of its three elements, Woehler's discovery is that urea and its derivatives are obtainable by synthesis. Since that date, hundreds of organic compounds have been produced wholly or partly by synthesis. By aid of the electric spark, carbon and hydrogen unite directly to acetylene, C_2H_2. Acetylene in presence of nascent hydrogen becomes ethylene, C_2H_4; this by incorporation of a molecule of water is converted to ethyl alcohol,

C_2H_5OH, and from this a host of other compounds usually reckoned as starch derivatives.

Moreover, acetylene $3(C_2H_2)$, when strongly heated, is condensed to benzene, C_6H_6. This is the starting-point from which the aromatic compounds are derived. These are so numerous as to require special treatises, and include such well known substances as benzoic and salicylic acids, aniline, and indigo.

569. The compounds which have been obtained from plants contain: (1) Only carbon and hydrogen; as, turpentine, $C_{10}H_{16}$. Or (2) more frequently, carbon, hydrogen, and oxygen; as, cellular tissue and starch, $C_6H_{10}O_5$; grape-sugar, $C_6H_{12}O_6$; and the fats; as, tri-stearin $C_3H_5(C_{18}H_{35}O_2)_3$. Or (3) they are nitrogenous substances like glue and albumin, nearly represented by the formula, $C_{72}H_{118}N_{18}O_{22}S$. But (4) intimately mixed with these are complex substances containing small quantities of phosphorus; as, lecithin. These four classes of bodies contain but six elements; but besides these, others are found in the ashes both of plants and animals, such as Ca, Na, K, Cl, F.

570. Any element may become associated with carbon in compounds which any chemist would class as *organic:* as chloroform, $CHCl_3$, zinc ethyl $(C_2H_5)_2Zn$. These artificial compounds are daily increasing in number, and are often of great theoretical interest, inasmuch as they are important factors in promoting chemical changes, and often indicate, with greater or less clearness, the structure of complex molecules.

571. The simplest saturated compounds of tetravalent carbon are marsh gas, CH_4; carbonic anhydride, CO_2; carbonic disulphide, CS_2; and prussic acid, HCN. Any one of these may be regarded as a source from which numerous compounds are derived. It is often possible to arrange these compounds in series which exhibit a

regular increase in vapor density, in boiling and melting points, etc. Those that are near each other in the series are always very much alike, but, of course, the differences increase with wider separation, and the remote members of a series are physically quite unlike.

HYDROCARBONS.

The following table exhibits portions of several series of saturated hydrocarbons. The number of terms known to be possible in each is about thirty, but no series is complete. The names after C_5 are usually formed from numerals, as hexane, heptane, octane, etc.

PARAFFINS.	OLEFINES.	ACETYLENES.	VALYLENES.	
Methane, CH_4	*Wanting*, CH_2	 C	. . . .	. . . .
Ethane, C_2H_6	Ethene, C_2H_4	Acetylene, C_2H_2	. . . . C_2	. . . .
Propane, C_3H_8	Propene, C_3H_6	Allylene, C_3H_4	*Propone*, C_3H_2	. . . . C_3
Butane, C_4H_{10}	Butene, C_4H_8	*Butine*, C_4H_6	*Butone*, C_4H_4	*Butune*, C_4H_2
Amane, C_5H_{12}	Amene, C_5H_{10}	Pentine, C_5H_8	Valylene, C_5H_6	*Pentune*, C_5H_4
Hexane, C_6H_{14}	Hexene, C_6H_{12}	Hexine, C_6H_{10}	*Hexone*, C_6H_8	Dipropargyl, C_6H_6
GENERAL FORMULA $\}$ C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n-4}	C_nH_{2n-6}

Names in italics indicate unknown members.
In general formulæ n stands for any number, and m for a number one less than n.
The members of the series arranged vertically differ by CH_2, and form *homologous series*.
The terms obtained by reading to the right differ by H_2, and form *isologous series*.

572. Any saturated hydrocarbon may be the starting-point from which other compounds are derived by the substitution of other radicals in place of one or more hydrogen atoms. Thus from ethane, C_2H_6, or its *hydride*, C_2H_5H, *its haloid derivative*, as C_2H_5Cl, *its hydroxide*, C_2H_5OH, *its oxide* $(C_2H_5)_2O$, etc. A selection of such derivatives constitutes a *heterologous* series.

573. Each homologous series is supposed to increase by substituting the univalent radical methyl, CH_3, for one of the H atoms in the preceding term. The effect of this is to increase the term by CH_2, as if the divalent radical methane had been inserted between two carbon atoms. This fact will be rendered clear by a few graphic formulæ:

Methane, CH_4 is $H \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot H$. The first substitution of CH_3 for H gives *ethane*, C_2H_6, or $H \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot H$, which might also be written C_2H_5H, and called ethyl hydride, or as $CH_3 \cdot CH_3$, and called di-methyl.

The next substitution gives C_3H_8, *propane*, $H \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot H$, or $CH_3 \cdot CH_2 \cdot CH_3$, or C_3H_7 H, propyl hydride, and also $CH_3 \cdot C_2H_5$, methyl-ethyl.

Butane is $C_4H_{10} = H \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot \begin{array}{c}H\\ \cdot\\ C\\ \cdot\\ H\end{array} \cdot H = CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$, or it is butyl hydride, C_4H_9H, or methyl propyl, $C_3H_7 \cdot CH_3$, or di-ethyl, $C_2H_5 \cdot C_2H_5$.

Dissected formulæ like these are of great service, and the student should accustom himself to consider that the radicals which are represented in them are actual entities as much so as an atom of chlorine or of sodium.

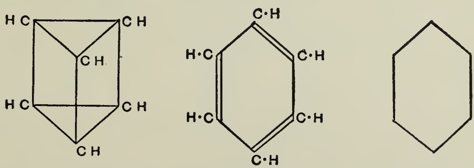
574. Whenever two carbon atoms unite, at least two "bonds" must become satisfied. The maximum combining power of *n*, carbon atoms, is C_nH_{2n+2}, which is that of the paraffin series. Such unions must always go by pairs, and the number of hydrogen atoms in any saturated hydrocarbon must be an even number.

In the *olefine* series, C_nH_{2n}, the first two carbon atoms must be doubly joined, as ethylene, C_2H_4, or $CH_2 = CH_2$; propene, C_3H_6, or $CH_2 = CH \cdot CH_3$; butene, C_4H_8, or $CH_2 = CH \cdot CH_2 \cdot CH_3$, and the succeeding terms by an increase of CH_2, as previously described. The *acetylene* series, C_nH_{2n-2}, has two carbon atoms trebly joined; as,

acetylene, $H \cdot C \equiv C \cdot H$, or $CH \equiv CH$, and allylene, $HC \equiv C \cdot CH_3$.

It will be noted that methyl, CH_3, ends most of these formulæ. It is supposed to be peculiarly susceptible of chemical change. The radical at the other end, CH_3, or $CH_2 = CH$, or $CH \equiv C$., may be regarded as the *nucleus* about which the complete molecule is gathered.

575. The aromatic hydrocarbons start from benzene, which is thought to contain six CH groups of equal chemical activity. This idea finds expression in various glyptic formulæ which represent the carbon atoms united in "closed chains," $(\equiv CH)_6$, as:



Any hydrogen atom in these may be replaced by CH_3, or by any other monovalent radical. In this way one or several "open" chains may be added to the benzene nucleus; as, C_6H_5, CH_2OH = benzene alcohol,

or C_6H_4, $(COOH)_2$, phthalic acid.

These compounds will be considered in Chapter XXVI.

The conception of open and closed chains, and a modification known as a "cleft" chain, is often serviceable in tracing chemical changes in complex compounds; but the student must remember that glyptic formulæ, and even rational formulæ, are attempts to represent to the eye the *facts* ascertained in chemistry. They are useful, because they enable the student to group together a large number of facts, and to frame theories which afford a satisfactory explanation of many such groups; but it can not be claimed for them that they are in any sense a picture of the molecular structure of any compound whatever.

576. Any member of any series of saturated compounds may be taken as the source from which radicals are derived by removal of one or more hydrogen atoms. The paraffin series may be made to yield the radicals shown in the table on p. 291.

577. Bodies are classed as saturated if they can exist in the free state, and if they form compounds with chlorine, etc., only by *substitution*, or, in a narrower sense, if all their theoretical "bonds" are satisfied. They are classed as *radicals* if they can not exist in the free state, but form stable compounds by combining with themselves; as, $CH_3 \cdot CH_3$, dimethyl; and if they form compounds with chlorine, etc., by *addition*. We know of compounds obtained from ethylene, C_2H_4 (which exists in the free state) of the formulæ, C_2H_3Cl; $C_2H_2Cl_2$, which are "substitution" products, and also an "addition" product, $C_2H_4Cl_2$. Hence, hydrocarbons, which contain an even number of hydrogen atoms, such as the olefines, may act as saturated molecules or as artiad radicals. In the latter case they are said to "open" their bonds,

$$CH_2 : CH_2 + Cl_2 = CH_2Cl \cdot CH_2Cl,$$

which is the same as saying that they revert to the preceding series.

578. Every hydrocarbon must be a radical if it contains an odd number of hydrogen atoms. The olefines

HYDROCARBON RADICALS.

PARAFFINS.	MONADS.	DYADS.	TRIADS.	TETRADS.	PENTADS.	HEXADS.
CH_4	CH_3	CH_2	CH	C	. . .	. . .
methane	methyl	methene	methenyl	. . .	. . .	. . .
C_2H_6	C_2H_5	C_2H_4	C_2H_3	C_2H_2	C_2H	C_2
ethane	ethyl	ethene	ethenyl	ethine	ethinyl	. . .
C_3H_8	C_3H_7	C_3H_6	C_3H_5	C_3H_4	C_3H_3	C_3H_2
propane	propyl	propene	propenyl	propine	propinyl	propone
C_4H_{10}	C_4H_9	C_4H_8	C_4H_7	C_4H_6	C_4H_5	C_4H_4
butane	butyl	butene	butenyl	butine	butinyl	butone
C_5H_{12}	C_5H_{11}	C_5H_{10}	C_5H_9	C_5H_8	C_5H_7	C_5H_6
amane	amyl	amene	amenyl	amine	aminyl	amone
etc.	etc.	etc.	etc.	etc.	etc.	etc.
C_nH_{2n+2}	C_nH_{2n+1}	C_nH_{2n}	C_nH_{2n-1}	C_nH_{2n-2}	C_nH_{2n-3}	C_nH_{2n-4}

The artiad radicals of this table are identical in form with the olefines and acetylenes.
The perissad radicals are never found free.

and acetylenes furnish perisad radicals similar in formulæ to those of the paraffins; but of course different in properties; thus, C_3H_5 represents the trivalent propenyl, the third derivative from propane, C_3H_8, and also the univalent allyl, the first derivative from propene, C_3H_6.

579. **Most organic compounds,** whose molecular structure is known, may be considered to be derived from the hydrocarbons. Such organic compounds, when once formed, are *units*, and may give rise to other series of radicals. Any saturated compound whatever may be divided in theory (that is, on paper) into any two parts. Each of these will be a radical, and each have the same valency. None of these radicals are of use, except those *which express some fact* observable in the formation of a compound or in its subsequent reactions.* Acetic acid is a good illustration. Its percentage composition is very well expressed by the empirical formula, CH_2O, but its vapor density (30) requires a molecular formula double that, or $C_2H_4O_2$. Its first rational formula, $H \cdot C_2H_3O_2$, expresses the fact that one of its hydrogen atoms is replaceable by the metals, as in silver acetate $AgC_2H_3O_2$; the second, $C_2H_3O \cdot OH$, that the haloid elements may displace hydroxyl, as in acetyl chloride, $C_2H_3O \cdot Cl$; the third, CH_3CO_2H, that it may be obtained from marsh gas, CH_3H, and furnish it; the fourth, that the carbonyl CO and hydroxyl OH act separately; the formula which represents most of these facts is:

$$CH_3 \cdot CO \cdot OH, \text{ or } CH_3, COOH.$$

580. **A radical** is simply the residue which is left of a body after undergoing a chemical change. Thus we

* In the following chapters the ethane, C_2, compounds will be taken when possible, partly because they are better known, and partly to accumulate examples to familiarize the student with organic transformations. He must keep constantly in mind that, *caeteris paribus*, analogous facts are true of similar bodies, Na and K; Cl and Br; O and S; P and As; $(CH_3)'$, $(C_2H_5)'$, and $(C_6H_5)'$; or CH_2OH, and CH_2SH.

may believe from the foregoing that acetic acid contains basic and acid hydrogen, H, hydroxyl, OH, carbonyl, CO, carboxyl, COOH, methyl, CH_3, and acetyl, C_2H_3O, because each one of these can be exchanged for or combined with other radicals or the elements, although no one of them has been isolated except CO in carbonous oxide.

Isomerism.

581. Two or more compounds which contain the same elements, and have the same percentage composition, but differ in properties, are said to be *isomeric*. There are several varieties of *Isomerism*:

1. Bodies are *physically* isomeric when they differ only in certain physical properties, as their odors or their relation to polarized light. Over twenty volatile oils have the composition, $C_{10}H_{16}$ (lemons, orange, bergamotte).

2. Bodies are *isomeric* in the strict sense of the word when they have the same vapor density, the same percentage composition, and exhibit similar chemical changes under similar circumstances. Thus there are two primary butyl alcohols which are strictly isomeric:

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH, \text{ and } \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot CH_2OH,$$

and which give rise to other compounds, acids, ethers, etc., which are also isomeric.

3. In the *general use* of the word, metameric bodies are also called isomers. Bodies are *metameric* when they have the same percentage composition and the same molecular weight, but exhibit dissimilar chemical properties under similar circumstances.

Propionic acid, methyl acetate, and ethyl formate have the same molecular formula, $C_3H_6O_2$, but when acted upon by caustic potash yield very dissimilar products:

The first, water and potassium propionate,

$$CH_3 \cdot CH_2 \cdot COOH + KOH = H_2O + CH_3 \cdot CH_2 \cdot COOK:$$

the second, methyl alcohol and potassium acetate,

$$CH_3 \cdot O \cdot C_2H_3O + KOH = CH_3OH + CH_3COOK:$$

the third, ethyl alcohol and potassium formate,

$$C_2H_5O \cdot O \cdot CHO + KOH = C_2H_5OH + H, COOK.$$

These reactions point to differences of structure within the molecules, which are approximately represented by formulæ like those above.

Some metamers are so totally different that no resemblances of structure have been imagined to exist. Such are starch and gum arabic, which are *pseudo-isomers.*

Metamers are found in all terms above C_3, and increase in number very rapidly with each addition of CH_2. There are four butyl alcohols known, two primary, which are strictly isomeric with each other, and two others metameric with these, which do not form corresponding acids and ethers.

4. *Polymeric bodies* agree in percentage composition, but do not have the same molecular weight. Their formulæ are multiples of some empirical formulæ common to all, as the CH_2 in the olefines, C_nH_{2n}.

582. There are more than twenty compounds which yield on analysis C,39.82%, H,6.75%, O,53.43%, corresponding to the empirical formula, CH_2O. The following table gives some of them:

CH_2O = $H \cdot CHO$, formic aldehyde.

$C_2H_4O_2 = \begin{cases} CH_3 \cdot O \cdot CHO, \text{ methyl formate.} \\ CH_3 \cdot COOH, \text{ acetic acid.} \end{cases}$

$C_3H_6O_3 = \begin{cases} (H \cdot CHO)_3, \text{ para formic aldehyde.} \\ CH_3 \cdot O \cdot CH_2 \cdot COOH, \text{ methyl glycollic acid.} \\ CH_3 \cdot CHOH, COOH, \text{ ethylidene lactic acid.} \\ CH_2OH \cdot CH_2 \cdot COOH, \text{ ethylene lactic acid.} \end{cases}$

$C_4H_8O_4$ — erythrite aldehyde?

$C_5H_{10}O_5$ — wanting.

$$C_6H_{12}O_6 = \begin{cases} (HCHO)_6, \text{ meta formic aldehyde.} \\ CH_2OH(CHOH)_4CHO, \text{ glucoses} \cdot \text{dextro and lævo.} \\ C_6H_6(OH)_6, \text{ phenose.} \end{cases}$$

The groups $(CH_2O)_n$ are *polymeric* with each other; the three aldehydes are stictly polymeric. The members of each group are *isomers* in the general sense. Some are *strictly isomeric*, as the two lactic acids, and some are *metameric*, as a lactic acid and methyl glycollic acid.

There are also two modifications of ethylidene lactic acid which contain the same radicals, and are chemically identical, but they differ in their relations to polarized light, and are *physical isomers*. The chemical structure of these molecules is the same, but the molecules have a different arrangement among themselves.

Classes of Organic Compounds.

583. The hydrocarbons contain carbon and an even number of hydrogen atoms. They include the paraffins, olefines, benzenes, and representatives of a dozen other series. It is sometimes convenient to write them as hydrides; that is, as having replaceable hydrogen, as $C_2H_5 \cdot H$, ethyl hydride, but more frequently as made up of compound radicals called *alkyls*, as

$$CH_3 \cdot CH_3 = \text{dimethyl}.$$

584. The alcohols are hydroxides of these hydrocarbon radicals, formed, as may be supposed, from the hydrocarbons by the substitution of hydroxyl for hydrogen, as ethyl hydroxide, C_2H_5OH, from ethyl hydride, $C_2H_5 \cdot H$. The methyl or "carbinol" series of alcohols contain but one hydroxyl group, as the ordinary or ethyl alcohol, C_2H_5OH. Such alcohols are *monohydric*. There are other series of alcohols which contain two, three, or more hydroxyl groups. Dyad radicals yield dihydric alcohols, or *glycols*, as $C_2H_4(OH)_2$, ethene glycol; and triad radicals, the trihydric *glycerols*, as $C_3H_5(OH)_3$,

commonly known as glycerine. The London Chemical Society recommends that all alcohols take the termination *ol*.

585. The normal alcohols take their names very generally from those of the radicals given on p. 291, as

methyl alcohol, $C\ H_4\ O = C\ H_3\ OH = H.CH_2OH.$
ethyl alcohol, $C_2H_6\ O = C_2H_5\ OH = C\ H_3 \cdot CH_2OH.$
propyl alcohol, $C_3H_8\ O = C_3H_7\ OH = C_2H_5 \cdot CH_2OH.$
butyl alcohol, $C_4H_{10}O = C_4H_9\ OH = C_3H_7 \cdot CH_2OH.$
amyl alcohol, $C_5H_{12}O = C_5H_{11}OH = C_4H_9 \cdot CH_2OH.$
hexyl alcohol, $C_6H_{14}O = C_6H_{13}OH = C_5H_{11} \cdot CH_2OH.$

The first two alcohols have no isomers; propyl has two; butyl, four; after this the numbers of alcohols theoretically possible increase very rapidly, being for amyl 8, hexyl 17, heptyl 39, octyl 78.

The isomeric alcohols present many points of peculiar interest, and are divided into three classes.

1. The *primary alcohols*, which may be oxidized, first, to aldehydes, and then to acids, which contain the same number of carbon atoms. These alcohols are supposed to contain the monovalent radical, CH_2OH, as a terminal group, *e. g.*, normal butyl alcohol,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH.$$

2. The *secondary alcohols* are supposed to contain a divalent radical, CHOH, *e. g.*, secondary butyl alcohol, $CH_3 \cdot CHOH \cdot C_2H_5$. Oxidizing agents convert this radical to CO, and the alcohol to a ketone, as methyl ethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$.

3. The *tertiary alcohols*, when oxidized, are completely broken up, yielding neither aldehydes nor ketones, but two acids containing each a less number of carbon atoms. These are supposed to contain the trivalent radical, $\equiv$COH, united to three other carbon atoms, as in tertiary butyl alcohol.

$$\begin{matrix}CH_3\\CH_3\end{matrix}>COH\cdot CH_3, \text{ or } CH_3, CH_3\cdot COH\cdot CH_3.$$

NOTE.—A comma placed between two radicals indicates that both are equally joined to the following group. The dot (or dash) indicates that they are joined to each other.

586. The different behavior of these alcohols upon oxidation is due to three different class radicals, $(CH_2OH)'$, $(CHOH)''$, and $(COH)'''$; but there are also other differences resulting from the structure of the nuclei. *Normal* alcohols are those in which no carbon atom is more than doubly united to another carbon atom, as normal butyl primary alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$. The *iso* alcohols have at least one carbon atom united to three other carbon atoms; as, isobutyl primary alcohol:

$$\begin{matrix}CH_3\\CH_3\end{matrix}>CH\cdot CH_2OH \text{ or } CH_3, CH_3\cdot CH\cdot CH_2OH.$$

587. Many organic acids are formed by the oxidation of the primary alcohols; the radical CH_2OH becoming $COOH$. The primary "methyl" alcohols give rise to the "fatty" acids; as

CH_2O_2	formic acid,	$CHO\cdot OH$ or $H\cdot COOH$.
$C_2H_4O_2$	acetic acid,	$C_2H_3O\cdot OH$ or $CH_3\cdot COOH$.
$C_3H_6O_2$	propionic acid,	$C_3H_5O\cdot OH$ or $C_2H_5\cdot COOH$.
$C_4H_8O_2$	butyric acid,	$C_4H_7O\cdot OH$ or $C_3H_7\cdot COOH$.
$C_5H_{10}O_2$	valeric acid,	$C_5H_9O\cdot OH$ or $C_4H_9\cdot COOH$.
. . .		
$C_nH_{2n}O_2$	general formula,	$C_nH_{2n-1}O\cdot OH$ or $C_nH_{2n+1}\cdot COOH$.

The formulæ in the second column represent that hydroxyl is united to an acid radical; as, formyl, CHO, acetyl, C_2H_3O, etc. Those in the third, that carboxyl, $COOH$, is united to an alkyl radical; as, CH_3, C_2H_5, etc.

588. The aldehydes are the first products obtained by oxidizing the primary alcohols; as,

$$CH_3\cdot CH_2OH+O=H_2O+CH_3\cdot HC:O=\text{ethyl aldehyde.}$$

They are unstable bodies, readily changing to the corresponding acids; as,

$$CH_3 \cdot HC:O + O = CH_3 \cdot COOH = \text{acetic acid.}$$

In the aldehyde radical, the carbon is directly united both to the hydrogen and to the oxygen.

589. In the ketones the group (CO)″ links together two univalent alkyl radicals which may be the same or different; as, acetone, $CH_3 \cdot CO \cdot CH_3$, methyl-ethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$. The ketones are generally obtained by the destructive distillation of the lime salts of the fatty acids: $(C_2H_3O_2)_2Ca = CaCO_3 + (CH_3)_2CO =$ acetone, but also, by the oxidation of the secondary alcohols,

$$\begin{matrix}CH_3\\CH_3\end{matrix} > CHOH + O = H_2O + \begin{matrix}CH_3\\CH_3\end{matrix} > CO$$

Isopropyl alcohol. Acetone.

The ketones are analogous to the aldehydes, and every ketone has some aldehyde metameric with it, as acetone is metameric with propyl aldehyde ($C_2H_5 \cdot CO \cdot H$).

590. The ethers include several classes of alkyl derivatives.

1. All alcohols exchange their hydroxyl for chlorine, bromine, or iodine, and form *haloid ethers*, which are primary, secondary, and tertiary, like the alcohols from which they derived, as the four butyl iodides, C_4H_9I:

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$; $CH_3 \cdot CH_2 \cdot CHI \cdot CH_3$.
$CH_3, CH_3 \cdot CI \cdot CH_3$; $CH_3, CH_3 \cdot CH \cdot CH_2I$.

With these are usually grouped the cyanogen ethers, as C_2H_5CN, ethyl cyanide.

NOTE.—The tertiary alcohol radical COH, contains hydroxyl, and is trivalent. The radical, formyl HCO, contains no hydroxyl, and is identical with the aldehyde radical, which, however, is not *formyl*. Compare formic acid, $H \cdot CO \cdot OH$.

2. *The simple ethers* are formed by removing one molecule of water from two molecules of an alcohol: as,

$$2(C_2H_5OH) - H_2O = C_2H_5 \cdot O \cdot C_2H_5 = \text{ethyl ether.}$$

They contain two similar alcohol radicals united by a linking oxygen atom.

3. *The mixed ethers* contain two different alcohol radicals united by oxygen; as,

$$CH_3 \cdot O \cdot C_2H_5 = \text{methyl-ethyl ether.}$$

The simple and mixed ethers are anhydrous oxides of the alcohol radicals. There are also sulphur ethers, etc.; as, $C_2H_5 \cdot S \cdot C_2H_5$, ethyl sulphide.

4. The substances commonly known as *compound ethers* contain both an acid and an alcohol radical linked by oxygen; as,

$$C_2H_5 \cdot O \cdot C_2H_3O = \text{acetic ether, or ethyl acetate.}$$

They are *ethereal salts*, and may be produced by the action of the oxy-acids upon the alcohols; as,

$$C_2H_5OH + NOOH = H_2O + C_2H_5 \cdot O \cdot NO = \text{ethyl nitrite.}$$

All compound ethers are easily broken up into alcohol and acid by heating them with water: more easily in the presence of a strong base like the alkalies; as,

$$C_2H_5 \cdot O \cdot C_2H_3\,O + KOH = C_2H_5OH + CH_3COOK.$$

This process is called *saponification*, a term originally applied in the manufacture of soap from neutral fats, which are compound ethers of glycerine.

591. The metals also combine with the alkyl radicals; as, $Zn(CH_3)_2$, *zinc methide* obtained by heating methyl iodide with zinc, $2CH_3I + 2Zn = ZnI_2 + Zn(CH_3)_2$. These must be distinguished from the *alcoholates* obtained by dropping sodium or potassium into absolute alcohol $C_2H_5OH + Na = \hat{H} + C_2H_5ONa$.

592. The ammonia derivatives have already been mentioned on page 130.

The organic amines contain alkyl radicals in place of one, two, or all of the hydrogen atoms in ammonia. Accordingly they form primary, $(NH)_2'$; secondary, $(NH)''$; and tertiary, $(N)'''$ amines; as,

$$\underset{\text{Ammonia.}}{N\begin{cases}H\\H\\H\end{cases}} \quad \underset{\text{Ethyl amine.}}{\overset{\text{Primary.}}{N\begin{cases}C_2H_5\\H\\H\end{cases}}} \quad \underset{\text{Diethyl amine.}}{\overset{\text{Secondary.}}{N\begin{cases}C_2H_5\\C_2H_5\\H\end{cases}}} \quad \underset{\text{Triethyl amine.}}{\overset{\text{Tertiary.}}{N\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases}}}$$

All amines strongly resemble ammonia in odor, in alkaline reaction, and in basic character. They unite directly with acids; as,

$N(C_2H_5)_3HCl$, triethyl ammonium hydrochloride,

and also form hydroxides; as,

$N(C_2H_5)_4OH$, tetrethylammonium hydroxide,

which are even more stable and caustic than ammonium hydroxide, NH_4OH.

593. The amides are also derived from ammonia, but by substitution of an acid radical for a part of its hydrogen. They also form three classes — primary, secondary, and tertiary — according as $\frac{1}{3}$, $\frac{2}{3}$, or $\frac{3}{3}$ of the hydrogen has been removed; as,

$$\underset{\text{Ammonia.}}{N\begin{cases}H\\H\\H\end{cases}} \quad \underset{\text{Acetamide.}}{N\begin{cases}C_2H_3O\\H\\H\end{cases}} \quad \underset{\text{Diacetamide.}}{N\begin{cases}C_2H_3O\\C_2H_3O\\H\end{cases}} \quad \underset{\text{Triacetamide.}}{N\begin{cases}C_2H_3O\\C_2H_3O\\C_2H_3O\end{cases}}$$

The primary amides have a feebly basic character; the others are feebly acid.

The alkalamides are secondary and tertiary ammonia

derivatives, containing both positive and negative radicals, as ethyl acetamide, $N(C_2H_5), (C_2H_3O), H$.

594. It will readily be seen that an enormous number of these compounds may be formed, and also that there can not fail to be numerous isomers. Thus, the empirical formula, NC_3H_9, represents four isomers, which are good examples of the value of structural formulæ:

$$N\left\{\begin{array}{l} CH_2\cdot CH_2\cdot CH_3 \\ H \\ H \end{array}\right. \qquad N\left\{\begin{array}{l} CH<\begin{array}{l}CH_3\\CH_3\end{array} \\ H \\ H \end{array}\right.$$

Propylamine. Isopropylamine.

$$N\left\{\begin{array}{l} C_2H_5 \\ CH_3 \\ H \end{array}\right. \qquad N\left\{\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right.$$

Ethyl-methyl-amine. Tri-methyl-amine.

595. The imides are secondary amides containing imidogen, $(NH)''$ united to a diatomic acid radical, as: succinimide, $C_2H_2O\cdot NH\cdot C_2H_2O$.

The nitriles contain trivalent nitrogen, united to a trivalent hydrocarbon radical, as CH. The first of these is methenyl nitrile, $CH\equiv N$, which has the same empirical composition as prussic acid, H, CN.

Action of Chemical Re-agents.

596. The number and variety of organic compounds is amazing, and it is almost impossible to describe them without a wearisome monotony. The *series* differ in marked peculiarities; but the members of any series differ gradationally, being, as a rule, progressively gases, liquids, and solids, normally increasing in density and also in boiling and in melting points. Those of the same group resemble each other in physical properties, like taste, odors, etc.

597. Many organic compounds may be distilled or sublimed unchanged, as ether, oxalic acid. At high temperatures they usually decompose; sometimes with simple reactions; as, oxalic acid, $2(COOH)_2$, strongly heated $=$ $H_2O + CO + 2CO_2 + H, COOH =$ formic acid. Generally they yield a variety of complex products and a residue of coke. Heated in the air they undergo the changes of ordinary combustion.

598. The usual re-agents produce in organic bodies the ordinary combinations, substitutions, and double decompositions, and always in accordance with the law of equivalent valency.

The oxygen of the air, at ordinary temperatures, has little effect upon most saturated organic compounds. Unsaturated compounds, like aldehydes and weak aqueous solutions of the alcohols, rapidly oxidize. The influence of oxygen in putrefaction and fermentation will be considered in another place. Moderate oxidation of organic bodies is effected by nascent oxygen usually obtained by mixtures of sulphuric acid with potassium bichromate (CHROMIC MIXTURE), or with manganese dioxide. The caustic alkalies and moist silver oxide are excellent oxidizing agents for the aldehydes and the polyhydric phenols.

Ordinary nitric acid is used as an oxidizing agent, or like any other acid, to form salts and ethers. The fuming acid acts often with great violence upon organic bodies, forming substitution products in which the radical nitryl $(NO_2)'$ replaces hydrogen, as benzene $= C_6H_6 + HNO_3 = H_2O + C_6H_5NO_2 =$ nitrobenzene. Such nitro substitution compounds are converted by nascent hydrogen to amines, as $C_6H_5NO_2 + H_6 = 2H_2O + C_6H_5NH_2 =$ *aniline.*

599. Oxygen compounds may lose the elements of water, $H \cdot O \cdot H$, when heated with P_2O_5, $ZnCl_2$, or with strong H_2SO_4, as $C_2H_5OH + H_2SO_4 = H_2SO_4 + H_2O + C_2H_4$. Conversely a prolonged boiling with weak sulphuric acid causes the assumption of water, as cane sugar,

$$C_{12}H_{22}O_{11} + H_2O \text{ is changed to } 2C_6H_{12}O_6 = \text{glucose.}$$

600. Nascent hydrogen is obtained in *acid* mixtures

from $Zn + H_2SO_4$, or on the larger scale from iron filings and acetic acid; in alkaline mixtures, from sodium amalgam. It acts reducing.

601. Free chlorine and bromine act energetically upon organic compounds.

(1) Removing hydrogen without replacement,

$$C_2H_5OH + Cl_2 = 2HCl + C_2H_4O = \text{aldehyde}.$$

(2) also replacing it, $CH_3COOH + Cl_2 = CH_2Cl, COOH + HCl$; and (3) by direct addition, $C_2H_4 + Cl_2 = C_2H_4Cl_2$; (4) in presence of water also acting oxidizing, $H_2O + Cl_2 = 2HCl + \widehat{O}$.

Iodine is less energetic, generally requiring the presence of a third body (as phosphorus) to form substitution products. So also hydriodic acid is somewhat different in action from either hydrobromic or hydrochloric acid.

602. The chemical changes by which a body is transferred from one series to another are always interesting and frequently of great importance. The following example is worthy study: (1) Marsh gas, CH_4, acted upon by Cl in the sunshine, yields CH_3Cl methyl chloride. (2) CH_3Cl, distilled with KOH, yields KCl, and $CH_3OH =$ methyl alcohol. (3) CH_3OH, distilled with strong H_2SO_4, yields $(CH_3)_2\ SO_4 =$ methyl sulphate. (4) $(CH_3)_2\ SO_4$, distilled with KCN, produces $2(CH_3CN)$ methyl cyanide. (5) This is identical with aceto nitrile C_2H_3N, a molecule containing two carbon atoms, and which, when acted upon by nascent hydrogen, becomes $C_2H_5NH_2$ ethyl amine. (6) Nitrous acid converts the amines to the corresponding alcohols; in this case to C_2H_5OH ethyl alcohol. (7) Ethyl alcohol, by oxidation, yields C_2H_4O aldehyde, and $C_2H_4O_2$ acetic acid. (8) Calcium acetate roasted yields acetone C_3H_6O, with three carbon atoms, etc., etc.

This example also shows how the chemist may pass from one carbon compound to the next higher in the same series, as from

methyl to ethyl alcohol; and it will be readily understood that other products belonging to other series may as readily be obtained. We shall now enter upon a study of some of the substances which are found in the various classes of organic compounds, neither attempting nor desiring to give so much as the names of the greater part of them. The selection which has been made contains those bodies which the student is likely to meet in his daily life.

As a rule only one process has been given for preparing these compounds, and that one generally selected for its theoretical importance rather than for its commercial value. In very many cases there are a dozen different processes for reaching the same result.

Recapitulation.

(1) A carbon atom is tetravalent, and is capable of combining with other carbon atoms.

(2) The hydrocarbons are typical compounds. Those containing an odd number of hydrogen atoms *must* be radicals; the others *may be*, except the paraffins.

(3) From these radicals may be formed *homologous* series, like the alcohols, the acids, the ethers, etc., whose members undergo the same kind of chemical transformations, but differ gradationally in their properties.

(4) These series are characterized by a common "class" radical, as OH in acids, alcohols, and phenols, COOH in acids, CH_2OH in primary alcohols, NH_2 in amides, or by a linking bond, as O or S in ethers, CO in aldehydes and ketones.

(5) In any series are members with isomeric modifications, which exhibit various degrees of similarity from the almost identical to a mere agreement in percentage composition.

(6) The isomers are supposed to be due (1) to a difference in the class radical, or (2) in the nucleus, or (3) to a difference in the physical arrangement of the molecules.

(7) Chemical forces produce in organic compounds the same changes as in inorganic, except that the range is wider.

(8) Any compound of carbon may be divided into two radicals of equal valency, which are residues of chemical reactions.

(9) That structural formula of a compound is most valuable which represents the largest number of chemical transformations of the given compound.

CHAPTER XVIII.

CYANOGEN COMPOUNDS.

603. Cyanogen gas was isolated by Gay Lussac, in 1815. It has a molecular density of 26, and being composed only of carbon and nitrogen, must have the molecular formula, $C_2N_2\left(\frac{12\times2+14\times2}{2}\right)$. It is interesting, as being the first example discovered of the existence of a free radical, which is in this instance the monovalent radical *cyanogen* $\cdot C{\equiv}N$ or Cy.

Cyanogen compounds are of frequent occurence in Nature, being easily obtainable from the leaves and kernels of stony fruited plants, like peaches and plums; as, HCN, prussic acid; and even from the human saliva, as, KCNS, potassium sulphocyanate. Potassium cyanide, KCN, is sometimes found in hearths of iron furnaces that use charcoal as fuel, being formed at high temperatures by the union of the nitrogen of the air blast with the carbon of the fuel and its potassium.

The same compound may be obtained by heating any nitrogenous body, like dried albumin, with a pellet of potassium. If the roasted mass be dissolved in water, filtered and treated when cold with a few drops of ferrous sulphate, partially changed to a ferric salt, and then neutralized with HCl, a precipitate of Prussian blue will be formed which contains $Fe_7(C_3N_3)_6$. This reaction is a very delicate test for nitrogen in such organic bodies.

604. Potassium ferrocyanide is manufactured by fusing together dried animal matters, such as scraps of leather, horn parings, etc., with potassium carbonate, and iron filings. The fused mass is cooled, then lixiviated with

hot water. On evaporating this solution, the salt crystallizes out in yellow quadratic prisms, $K_4FeC_6N_6 + 3H_2O$. This is the most convenient source for obtaining other cyanogen compounds.

I. Strongly heated alone it decomposes, yielding potassium cyanide, $K_4FeC_6N_6 = \widehat{N}_2 + C_2Fe + 4KCN$.

II. Strongly heated with potassium carbonate, it yields potassium cyanide, KCN; mixed with potassium cyanate, KCNO; thus,

$$K_4Fe(C_3N_3)_2 + K_2CO_3 = \widehat{CO}_2 + Fe + 5KCN + KCNO.$$

III. This product, by remelting with oxidizing agents, yields pure potassium cyanate; *e. g.*,

$$4KCN + Pb_3O_4 = Pb_3 + 4KCNO,$$

or (2) with reducing agents, like charcoal, yields pure potassium cyanide, $KCNO + C = \widehat{CO} + KCN$, or (3) if heated with strong sulphuric acid, yields hydrocyanic acid itself, $2(K_4Fe(C_3N_3)_2) + 3H_2SO_4 =$

$$K_2Fe_2(C_3N_3)_2 + 3K_2SO_4 + \overline{6H\widehat{C}N}.$$

It is advisable to moderate the action by the addition of about 20 parts of water. The hydrocyanic acid which forms may then be distilled over, mixed with water. *Exceeding care* must be used in its preparation, the receiver cooled with ice, and any uncondensed vapors completely carried away from the operator by a strong draught.

605. Anhydrous hydrocyanic acid, HCN, is a clear liquid, boiling at 26°C, congealing at —15°: sp. gr. 0.7. It decomposes spontaneously after a time, evolving odors of NH_3. Its aqueous solution is more stable; but even this, when boiled with acids or alkalies, is rapidly decomposed, yielding formic acid and ammonia,

$$HCN + 2H_2O + HCl = H, COOH + NH_3, HCl.$$

The officinal solution of the apothecary contains 2%

of the anhydrous acid, and has an odor resembling that of bitter almonds. In this dilute condition it is a valued medicine. The greatest caution is necessary in handling it, as it is one of the *most violent poisons known;* a single drop of the anhydrous acid being sufficient to cause death almost instantaneously. The metallic cyanides also yield HCN when treated with a dilute acid, and hence are often as poisonous as the acid itself.

606. The metallic cyanides are obtained by the action of hydrocyanic acid upon their oxides. The simple cyanides are analogous to the chlorides, the radical CN or Cy exactly taking the place of an atom of chlorine; *e. g.*,

$$HgO + 2HCl = H_2O + HgCl_2.$$
$$HgO + 2HCN = H_2O + HgC_2N_2.$$

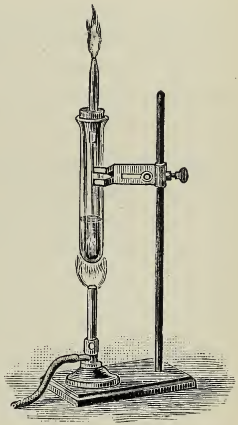


FIG. 101.

607. Cyanogen gas, C_2N_2, is formed when dry mercuric cyanide is strongly heated. It is a colorless, very poisonous gas, which has the odor of prussic acid, and burns with a fine peach-colored flame. It has a density of 1.86. It is easily condensed to a colorless liquid, sp. gr. 0.86, which boils at —21°C, and freezes to a crystalline mass at —34°C. Cyanogen gas passed into a solution of potassium hydrate yields potassium cyanide and potassium cyanate:

$$C_2N_2 + 2KHO = KCN + KCNO + H_2O.$$

The radical cyanogen is characterized by a great tendency to form polymeric compounds. Some are saturated, as cyanogen gas and paracyanogen, a brown substance, which forms, along with cyanogen, when HgC_2N_2 is heated. Others are complex radicals;

Divalent, $C_2N_2 = \begin{array}{c} \cdot C = N \\ \dot{} \quad \dot{} \\ N = C \cdot \end{array}$; trivalent, $C_3N_3 = \begin{array}{c} \cdot C = N \\ \dot{} \quad \dot{} \\ N - C \cdot \\ \dot{} \quad \dot{} \\ \cdot C = N \end{array}$

There are also metameric compounds in which the nitrogen acts pentavalent; as, iso-cyanogen and its polymers:

$C \equiv N \cdot R$, isocyanide; divalent, $\begin{array}{l} C \equiv N \cdot R; \text{ etc.} \\ R \cdot \dot{N} \equiv C \end{array}$

and pseudo-cyanogen and its polymers, in which the C and N are linked by two bonds, as in potassium cyanate,

$K \cdot N = C = O$, cyanate; divalent, $\begin{array}{c} K \cdot N \cdot C = O \\ O = \dot{C} \cdot \dot{N} \cdot K \end{array}$ etc.

There are also compounds of carbon and nitrogen, which contain two different forms of these.

Moreover, compounds based on these bodies readily change one into the other, and quite as readily decompose; the nitrogen producing ammonia; the carbon, formic, oxalic, and other acids.

608. Potassium cyanide, KCN, forms colorless cubical crystals, deliquescent, easily soluble in water, and exhaling the odor of hydrocyanic acid. This dilute solution rapidly decomposes to potassium formate and ammonia, $KCN + 2H_2O = NH_3 + H \cdot COOK$. Heated with the metallic oxides it melts easily, forming a fine flux, and also acts as a strong reducing agent, becoming itself oxidized to cyanate, $PbO + KCN = Pb + K \cdot CN \cdot O$.

The other alkaline cyanides resemble KCN. The cyanides of the heavy metals (except mercuric cyanide, HgC_2N_2) are insoluble in water, and may be prepared by mixing solutions of their salts with a solution of KCN, avoiding an excess. The most important are AgCN, NiC_2N_2, AuC_3N_3.

If an excess of KCN is used, most cyanides of the heavy metals unite with it to form double cyanides, which are easily soluble in water; as,

$$AgCN, KCN = \begin{array}{l} Ag \cdot C = N \\ \qquad \dot{N} = \dot{C} \cdot K. \end{array}$$

These double cyanides are easily decomposed by HCl, forming chlorides of the metals and setting free HCN. They are therefore poisonous. They have been extensively used in electroplating, because they yield by electrolysis the metals in strongly coherent films.

609. The cyanides of iron are difficult to obtain, because they so readily unite with other cyanides. In presence of an excess of KCN, they unite so intimately with it as to form, not double cyanides, but entirely new compounds, in which the iron does not respond to the ordinary tests, and which do not evolve HCN on being treated with cold dilute acids. The commercial manufacture of one of these, potassium ferrocyanide, has been given in § 604. The other is potassium ferri-cyanide, prepared by passing chlorine into a cold solution of potassium ferrocyanide until a drop of the liquid will no longer produce a blue precipitate with ferric chloride. On evaporating this solution, potassium ferri-cyanide, $K_3FeC_6N_6$, forms in ruby rhombic prisms:

$$2K_4FeC_6N_6 + Cl_2 = 2KCl + 2K_3FeC_6N_6.$$

The chlorine acts by removing a fourth part of the potassium, and by converting the iron from the ferrous (Fe'') to the ferric (Fe''') state. The ferri-cyanide in presence of alkaline hydrates acts oxidizing, and reverts to ferrocyanide. This property is utilized in calico printing, in which such a mixture is used as a discharge for indigo: $2K_3FeC_6N_6 + 2KHO = H_2O + 2K_4FeC_6N_6 + \widehat{O}$. The former is known as the yellow, and the latter as the red, prussiate of potassium. The yellow prussiate is extensively employed in the manufacture of dyes and paints, as Prussian blue and chrome green. The potassium in both these "prussiates" may be replaced by hydrogen or by the metals, leaving in both cases a residue of $Fe(C_3N_3)_2$, which, in the former, acts as an "ous" radical, tetravalent ferro-cyanogen, and, in the latter, as an

"ic" radical, the trivalent ferri-cyanogen. Their structural formulæ are here contrasted:

$$\equiv Fe < \begin{matrix} C_3N_3 < \begin{matrix} K \\ K \end{matrix} \\ C_3N_3 < \begin{matrix} K \\ K \end{matrix} \end{matrix} \qquad \equiv Fe \begin{matrix} \diagup C_3N_3 < \begin{matrix} K \\ K \end{matrix} \\ \diagdown\!\diagdown C_3N_3 \cdot K \end{matrix}$$

Potassium ferrocyanide. Potassium ferricyanide.

The hydrogen compounds, $H_4Fe(C_3N_3)_2$, hydro-ferrocyanic acid, and, $H_3Fe(C_3N_3)_2$, hydro-ferricyanic acid are unimportant. They are decomposed by long boiling, yielding, among the products, prussic acid, HCN.

610. The other ferrocyanides are formed by mixing solutions of potassium ferrocyanide with those of the other metals, producing compounds like the cupric ferrocyanides, $CuK_2FeC_6N_6$, and $Cu_2FeC_6N_6$, according as an excess of the one or the other solution is used. The ferricyanides are produced by analogous reactions, but obviously not in the presence of bodies like $SnCl_2$, which are easily oxidized; nor in the presence of strong alkalies, which decompose them.

Some of these reactions are valuable tests. Especial interest attaches to the reactions with salts of iron, already noted on page 266.

When oxygen is completely excluded, green ferrous sulphate yields with potassium ferrocyanide:

$$Fe''_2, Fe''\ (C_3N_3)_2, \text{ and } K_2Fe'', Fe''(C_3N_3)_2,$$

both speedily oxidize in the air, to Prussian blue,

$$Fe'''_4(Fe''C_6N_6)_3,$$

which forms immediately when ferric chloride is added to potassium ferrocyanide. An excess of the latter dissolves a portion of this, forming the so-called soluble Prussian blue.

With solutions of the ferri-cyanide, ferrous salts yield Turnbull's blue, $Fe''_3(Fe'''C_6N_6)_2$. Ferric salts yield no

precipitate unless some reducing agent is present, when a blue precipitate forms.

These beautiful blue colors are employed extensively in dyeing, and in the manufacture of paints. The ordinary blue ink is Prussian blue dissolved in oxalic acid.

Similar complex radicals containing Co, Mn, Pt, and Cr, in place of Fe, are known. Of these, potassium cobaltic-cyanide, $K_3CoC_6N_6$, is important, because, by forming it, a quantitative separation of cobalt from nickel may be effected. Cobalt also forms several series of complex cyanogen compounds which can not here be described.

611. Nitro prussides are formed by treating the alkaline ferrocyanides with fuming nitric acid. Potassium ferrocyanide so treated yields approximately:

$$K_4FeC_6N_6 + 3HNO_3 =$$
$$CO_2 + NH_3 + 2KNO_3 + K_2FeC_5N_5NO =$$
the nitro prusside of potassium.

In these compounds the radical *nitrosyl* is exchanged for one of cyanogen. The soluble nitro prussides are exceedingly delicate tests for the alkaline sulphides, with which they strike in dilute solutions a beautiful purple color.

612. Cyanogen forms, with the alcohol radicals, two series of ethers; the cyanides or nitriles, as ethyl cyanide, C_2H_5CN, and their metamers, the isocyanides or carbamines; as, ethyl isocyanide, C_2H_5NC. These compounds differ widely in their properties, and will be further considered.

Cyanogen also combines with the halogens, forming cyanogen chloride, CNCl, which is a liquid, and its polymer, $C_3N_3Cl_3$, which is a solid, and other compounds.

613. There are two isomeric potassium cyanates; the normal, obtained by passing the vapor of cyanogen chloride into potash lye:

$$CN \cdot Cl + 2KHO = KCl + H_2O + (C \equiv N) \cdot O \cdot K.$$

This changes, when melted, to the usual form, which is known as the iso-cyanate, or the pseudo-cyanate:

$$O=C=N \cdot K,$$

obtained as before noted by heating potassium cyanide with metallic oxides. Only one cyanic acid is known, CNOH, probably the normal acid, $N \equiv C \cdot O \cdot H$. It has several isomers. Cyamelide, a white amorphous mass into which it spontaneously changes. Cyanuric acid $(C_3N_3)(OH)_3$, which, when heated, becomes cyanic acid, and fulminic acid, $(C_2N_2)(OH)_2$, which has never been isolated, and fulminuric acid, $C_3N_3H_3O_3$, isomeric with cyanuric acid, but monobasic.

Ammonium isocyanate, $CN \cdot O \cdot NH_4$, produced when the dried vapors of cyanic acid, CNOH, and ammonia, NH_3, meet, is manufactured by decomposing lead cyanate with ammonium sulphate. This body is remarkable, because it passes spontaneously, even in the solid state (more rapidly on heating its solution), into urea, with which it is isomeric, $NH_2 \cdot CO \cdot NH_2$. Therefore, urea (1) can be made from ammonia plus cyanic acid. (2) If urea is heated, it breaks up into ammonia and cyanuric acid; but (3), if cyanuric acid is still further heated, it splits up into the original cyanic acid.

614. The fulminates of silver and of mercury are remarkable for the violence with which they explode on being struck. They are used for filling percussion caps. On the large scale, mercuric fulminate, $CHgNO_2CN$, is made by adding to one part of mercury 12 parts of nitric acid and 6 parts of alcohol. After the reaction begins other 6 parts of alcohol are added by degrees. Vapors of nitric ether, aldehyde, etc., are given off, and the mercuric fulminate forms in crystalline plates. These are purified by redissolving in hot water and recrystallizing. The greatest care is necessary in handling the dry salt, even in very small quantities.

Silver fulminate, CAg_2NO_2CN, is prepared in a similar manner. It is one of the most dangerously explosive compounds known.

615. Sulphocyanic acid, CNSH, is the analogue of cyanic acid, which it resembles. Its most important salt, potassium sulphocyanate, occurs in the saliva, and is easily formed by fusing together sulphur and potassium ferrocyanide. After cooling, the sulphocyanate is dissolved out with hot water and crystallized. Ammonium sulphocyanate is easiest made by warming alcoholic ammonia with carbon bisulphide,

$$2NH_3 + CS_2 = H_2S + NH_4CNS.$$

It has been proposed to use this reaction in purifying coal gas from CS_2.

The sulphocyanates of Cu, Pb, Ag, and Hg are produced by mixing salts of these metals with either of the preceding. Neutral ferric salts give no precipitate with them, but produce an intense blood-red color.

Conversely, these reactions serve for the detection of sulphur and of prussic acid.

(1) Sulphur, by heating the dried substance which contains it with KCN; extracting the sulphocyanate formed with hot water, filtering, and then testing with a dilute solution of ferric chloride. (2) Prussic acid, by exposing to its vapors, a drop of silver nitrate, white, AgCN, forms. On treating this with a small quantity of ammonium sulphide, black, AgS, and soluble ammonium sulphocyanate, NH_4CNS, are produced. This mixture is heated gently to expel the excess of NH_4HS, dissolved in water, filtered, and tested with ferric chloride.

Mercuric sulphocyanate, $(CNS)_2Hg$, has the curious property of enormously increasing in volume when ignited. It is used in the toy, Pharaoh's serpents.

616. The oil of mustard is allyl sulphocyanate,

$$C_3H_5CNS.$$

This can be made by decomposing allyl iodide, C_3H_5I, by an alcoholic solution of potassium sulphocyanate. A large number of similar compounds have been manufactured which are known collectively as the "mustard oils."

617. Tests. All cyanogen compounds may be made to yield Prussian blue. This may be effected generally by (1) boiling with KHO; (2) adding a crystal of effloresced $FeSO_4$; (3) filtering and then acidulating with HCl.

Recapitulation.

(1) CN is a negative, univalent radical, with three isomeric modifications. Each isomer has several polymers.

(2) The polymers are saturated; as, cyanogen gas, C_2N_2; or are radicals having a valency equal to the number of times the CN is taken; as, $(C_3N_3)'''$.

(3) The metallic cyanides contain one or several metals, forming single and double cyanides, easily decomposed, poisonous salts.

(4) CN also forms complex radicals; as, $(CNO)'$, $(CNS)'$, in potassium cyanate and sulphocyanate, and with NO_2 as $(C_5N_5NO_2)$ in the nitro-prussides.

(5) C_3N_3 forms with some metals aggregates which contain the metals in both the "ous" and "ic" states. These aggregates are complex radicals, like the ferro$''$, ferric$'''$ cyanogen.

(6) All these radicals form a series of salts with the metals which are derived in theory from an acid. Most of the acids are also known.

CHAPTER XIX.

THE HYDROCARBONS.

618. The hydrocarbons comprise a number of isologous series which differ by H_2; as, the paraffins, C_nH_{2n+2}; the olefines, C_nH_{2n}. The successive numbers of each of these differ by CH_2. The highest number known contains C_{32}, and we may expect that each series contains at least 32 members, but in no case have all the successive terms been isolated.

The members of each series exhibit properties which are strikingly gradational. The lowest members of each series, CH_4, C_2H_4, C_2H_2, are gases at ordinary temperatures. As the molecular weight increases there is an almost regular increase in vapor density and specific gravity, in boiling and in melting points. Those containing from 5 to 20 carbon atoms are generally liquids; the highest members are solids. The isomeric modifications are very numerous. It is possible to construct a *normal* and an *iso* series for the paraffins, olefines, and acetylenes, each with well characterized differences and resemblances.

All these hydrocarbons are capable of mixing perfectly together, the liquids absorbing the gases, dissolving one another and the solids. Such mixtures of hydrocarbons are found among the products of the destructive distillation of fatty bodies and of bituminous coal. Some are found native in petroleum, in Rangoon tar, etc.

All are inflammable, the olefines giving, perhaps, the brightest flame. Their vapors, mixed with air, form dangerously explosive mixtures; the more likely to be

produced from the lowest and more volatile members. Serious accidents from this cause are of very common occurrence.

619. **The paraffins,** C_nH_{2n+2}, are, for the most part, inert bodies, capable, however, of forming substitution products with the haloid elements; as,

$$CH_4 + Cl_2 = HCl + CH_3Cl.$$

These chlorides, etc., heated with alkaline hydrates, yield the corresponding alcohols,

$$CH_3Cl + KHO = KCl + CH_3OH.$$

They are obtained artificially from alcoholic haloides by the action of nascent hydrogen, $CH_3Cl + H_2 = HCl + CH_4$.

The crude petroleum of Pennsylvania is a mixture containing almost the entire series. The lighter gases readily escape, and the remaining liquid is subjected to a process of fractional distillation in iron retorts. The first products which are condensed only by freezing mixtures, are called cymogene and rhigolene. These are used only for producing artificial cold by their rapid evaporation. Next in order are liquids boiling below 100°C. Such as gasoline (used for gas-making), naphtha (used for paints and varnishes), and benzene or light oil (used for illuminating purposes in lamps without wicks). Then follow the ordinary coal-oils. "Paraffin," a thicker oil, used for lubricating; a very soft paraffin, "vaseline," used for pomades, etc.; a pliable paraffin, used for chewing gum; and the hard paraffin, melting about 40°C, used for candles. A residue of porous coke is left. All these substances are mixtures, the names given to them do not express constant composition. They are afterwards rectified by agitation with sulphuric acid (from 2% to 40%), which removes the olefines and some of the color, washed with water and with caustic soda to remove the last traces of acid. They are then ready for market.

Those "kerosines," which are sold for illuminating purposes, are graded by "the flashing test." This is variously defined by State laws, but usually means the temperature at which the vapors of the oil escape with sufficient rapidity to enkindle when a very small flame is held $\frac{1}{8}$ of an inch above the surface of the liquid. Ohio test, 110°F = 43°C. It is approximately, 20°C or 35°F, below

the "fire test," which is the temperature at which the oil burns. Of course the boiling point is much above either of these.

The "kerosines" are those paraffins that are distilled between 150° and 300°C. If properly manufactured, such oils are perfectly safe for household illumination. Unfortunately, at high temperatures, the complex paraffins have a tendency to "crack;" that is, to split up into several lower paraffins and olefines, so that even the heavy oils often contain a large amount of the lighter oils. It is also customary to prepare illuminating oils by mixing benzene with heavier products. These volatile products easily escape, and produce explosive mixtures with the air in the lamps. No oil is safe that flashes when a lighted match is held near it.

620. Methane, CH_4, also called marsh gas, from the fact that it may be obtained from stagnant marshy pools, is found in coal mines as "fire-damp," in the springs of inflammable gas common on the borders of Ohio and Pennsylvania, and forms about 80 per cent of ordinary coal gas. It is artificially prepared by heating an intimate mixture of dried sodium acetate with double its weight of soda-lime,

$$CH_3COONa + NaHO = CH_4 + Na_2CO_3.$$

Methane is a colorless, inodorous gas, about half as heavy as air, vapor density $= \frac{12+4}{2} = 8$. It burns with a yellowish flame, $CH_4 + O_4 = CO_2 + 2H_2O$, but when mixed with double its volume of oxygen, it enkindles with explosive violence.

Ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}, gases at ordinary temperatures, are found mixed with methane in the gases which escape in boring for petroleum. These wells have been used extensively for lighting villas and villages, for fuel in stoves and furnaces, and more recently for the manufacture of lampblack.

621. The olefines, C_nH_{2n}, afford an excellent example of a series of polymers, being all multiples of CH_2, methene. About 20 olefines are known, which, so far as they exist in the free state, are saturated compounds

capable of forming substitution compounds with chlorine, etc.; as, C_2H_3Cl = chlorethene.

The olefines also act as dyad radicals, directly uniting with the halogens and with concentrated sulphuric acid; as, $CH_2 : CH_2 + Cl_2 = CH_2Cl \cdot CH_2Cl$ or $C_2H_4Cl_2$, a pair of the "latent carbon bonds" opening for the Cl_2. They tend also to form polymers. For example: two molecules of amylene, C_5H_{10}, condense to one of decene, $C_{10}H_{20}$.

The only important olefine is ethylene, C_2H_4. It is prepared by heating alcohol with 6 times its weight of strong sulphuric acid, $C_2H_5OH—H_2O=C_2H_4$. (P. 323.) It was called *olefiant gas*, because it forms with Cl_2, an oily liquid, which is a diatomic haloid ether. (P. 395.)

Ethylene is a colorless, poisonous gas, condensable by pressure to a liquid which boils at —110°. Its vapor burns with a brilliant white flame. It and its homologues constitute the "illuminants" in ordinary coal gas, of which they form from 5% to 10%.

Propylene, C_3H_6, and butylene, C_4H_8, are also gases at ordinary temperatures. There are 3 butylenes and 4 amylenes known. The latter are liquids with boiling points between 25°C and 75°C.

622. The normal acetylenes (C_nH_{2n-2}) form crystalline precipitates when their vapors are passed into an ammoniacal solution of cuprous chloride. This precipitate treated with HCl yields the acetylene hydrocarbon in the pure state. It contains the trivalent, CH, as in the normal *allylene*, $CH \equiv C \cdot CH_3$. The isomers do not form the cuprous compound, and contain different radicals; as, *allene*, $CH_2 = C = CH_2$.

Acetylene, C_2H_2, or $CH \equiv CH$, is a colorless gas, of an unpleasant odor, which burns with a bright, but smoky, flame. It is a common product of the incomplete combustion of organic bodies.

It is easiest obtained by causing the gas in a Bunsen's burner to burn at the bottom of the tube. The products of the combustion are drawn by means of an aspirator through an ammoniacal solution of cuprous chloride. A red precipitate of di-acetylene—cuprous oxide—forms:

$$2C_2H_2 + 2Cu'_2Cl_2 + H_2O = 4HCl + CH \equiv C \cdot Cu_2 \cdot O \cdot Cu_2 \cdot C \equiv CH,$$

which is explosive when dry. This precipitate, treated with hydrochloric acid, yields pure acetylene:

$$C_4H_2Cu_4O + 4HCl = 2Cu_2Cl_2 + H_2O + \overline{2C_2H_2}.$$

The chief interest which attaches to acetylene arises from the fact that it is the only hydrocarbon which has been produced by direct union of its elements, and that from it may be derived, with greater or less trouble, an enormous number of carbon compounds.

623. Few hydrocarbons of the higher series have been isolated. The terpenes have the general formula, C_nH_{2n-4}; as, turpentine, $C_{10}H_{16}$, but they belong to the aromatic group. The general formula, C_nH_{2n-6}, includes two different bodies, di propargyl, $HC \equiv C \cdot CH_2 \cdot CH_2 \cdot C \equiv CH$, constructed as an "open chain," and benzene, C_6H_6, the first of the hydrocarbon series with closed chains, which will be considered among the aromatic compounds.

Recapitulation.

(1) The hydrocarbons all act as saturated bodies, containing an even number of hydrogen atoms.
(2) Such hydrocarbons as contain an odd number of hydrogen atoms are perissad radicals. So, also, many are known which act as artiad radicals.
(3) They may be arranged in homologous series, whose members differ successively by CH_2.
(4) Also, in isologous series, differing by H_2.
(5) They may be obtained by synthesis, but their chief sources are the natural oil wells and bituminous coal.
(6) They are employed (1) as refrigerants, (2) as illuminants, (3) as lubricants.
(7) The chief series are the paraffins, the olefines, and the benzenes.

CHAPTER XX.

THE ALCOHOLS.

624. All alcohols contain hydroxyl, and are defined to be hydroxides of hydrocarbon radicals; as, ethyl hydroxide, C_2H_5OH. They may be regarded as formed from saturated hydrocarbons by the substitution of hydroxyl for hydrogen. Thus, from propane, C_3H_8, are derived, C_3H_7OH, propyl alcohol; $C_3H_6(OH)_2$, propene alcohol; $C_3H_5(OH)_3$, propenyl alcohol.

Alcohols are classed, according to the number of hydroxyl groups they contain, into monohydric (OH), dihydric $(OH)_2$, trihydric $(OH)_3$, etc. It is proposed to use the termination *ol* for all these; as, monohydric = *alcohols;* dihydric = *glycols;* trihydric = *glycerols* and *pyrogallols;* hexhydric = *mannitols*, etc.

625. The monohydric alcohols include several series built up upon monovalent radicals; as, (1) from the paraffins, the *methyl* alcohols, or *carbinols*, $C_nH_{2n+2}O$, or $C_nH_{2n+1}OH$; (2) from the olefines, the *vinyl* alcohols, $C_nH_{2n-1}OH$, and others of the "open chain" sort. (3) The "closed chain" benzenes give rise to the benzyl alcohols,* $C_nH_{2n-7}CH_2OH$, and their isomers, the *phenols*, $C_nH_{2n-7}OH$, $(+ CH_2)$.

The polyhydric alcohols also contain different series, but these are not so well known, nor so distinctly classified as the monohydric. These alcohols increase gradually in sweetness until the hexhydric alcohols are reached.

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*These should be called the *benzoles*. Unfortunately the words benzole and benzene are applied both to the lighter paraffins, CnH_2n+_2, and to the first of the aromatic hydrocarbons, C_6H_6.

The mannitols, $C_nH_{2n-4}(OH)_6$, are natural alcoholic sugars; as, *mannite.*

The other sugars are related to these; but in what way has not been satisfactorily ascertained.

626. The carbinols, or the methylic series of alcohols, have been more thoroughly investigated than the others. The following table exhibits the best known members of the series.

ALCOHOLS.

	PRIMARY ALCOHOL.	ORDINARY SOURCE.	FORMULÆ.	BOILING POINT.	SP. GR. AT 15°.
C_1.	Methylic.	Distillation of wood.	$C\ H_3\ OH$.	66°.C.	0.798.
C_2.	Ethylic.	Fermentation of sugar.	$C_2\ H_5\ OH$.	78°.4.	0.794.
C_3.	Propylic.	Fusel-oil.	$C_3\ H_7\ OH$.	97°.4.	0.806.
C_4.	Butylic.	Fermentation of glycerine.	$C_4\ H_9\ OH$.	116°.9.	0.824.
C_5.	Amylic.	["Iso" in fusel-oil.]	$C_5\ H_{11}OH$.	137°.	0.817.
C_6.	Caproic.	Cow-parsnep.	$C_6\ H_{13}OH$.	157°.2.	0.833.
C_7.	Œnanthic.	Castor-oil.	$C_7\ H_{15}OH$.	175°.5.	0.830.
C_8.	Caprylic.	Cow-parsnep.	$C_8\ H_{17}OH$.	190°.	0.830.
. . .	. . .	. . .	. . .	Meltg. point.	. . .
C_{16}.	Cetylic.	Spermaceti.	$C_{16}H_{33}OH$.	50°.	. . .
. . .	. . .	. . .	. . .	. . .	. . .
C_{27}.	Cerylic.	Chinese-wax.	$C_{27}H_{55}OH$.	79°.	. . .
. . .	. . .	. . .	. . .	. . .	. . .
C_{30}.	Melissic.	Bees-wax.	$C_{30}H_{61}OH$.	85°.	. . .

627. The higher members have numerous isomers which are classified as primary, containing $(CH_2OH)'$; secondary, containing $(CHOH)''$; and tertiary alcohols, containing $(COH)'''$. These groups behave differently upon oxidation, and are, therefore, metamers. The primary have lower boiling points than the secondary, and these than the tertiary. The normal alcohols are of higher boiling points than their "iso" forms, etc.

Some of these alcohols exist free in nature, especially in plants of the parsnep family. Others are obtained by saponifying the natural ethers, like the oil of wintergreen; and some are obtained by synthetical operations. The process of fermentation, which is employed in making ordinary alcohol, not unfrequently yields also several alcohols. "Fusel-oil" is a mixture of the lower carbon alcohols, from propylic to caprylic.

628. All the anhydrous alcohols dissolve potassium and sodium with the formation of solid compounds called *alcoholates;* as, C_2H_5OK = potassium ethylate. These bodies readily exchange their metals for other equivalent radicals; as, $C_2H_5ONa + C_2H_5Cl = NaCl + C_2H_5 \cdot O \cdot C_2H_5$ = ethyl ether.

629. The alcohols act as weak compounds, readily combining with the acids, setting free a molecule of water, and forming the so-called "compound ethers;" *e. g.*,

$$CH_3OH + HONO = H_2O + CH_3 \cdot O \cdot NO = \text{nitrous ether.}$$

With polybasic acids, intermediate compounds may be also formed; thus, from ethylic alcohol and sulphuric acid may result:

(1) $C_2H_5OH + HO \cdot SO_2 \cdot OH = H_2O + C_2H_5O \cdot SO_2 \cdot OH$, acid ethyl sulphate.

(2) $(C_2H_5OH)_2 + HO \cdot SO_2 \cdot OH = 2H_2O + C_2H_5O \cdot SO_2 \cdot C_2H_5O$, ethyl sulphate. Both of these are produced in the manufacture

of "sulphuric ether" at temperatures below 154°C. Above this temperature results from the foregoing, either:

(3) $C_2H_5OH \cdot SO_2 \cdot OH + C_2H_5OH = (HO)_2SO_2 + (C_2H_5)_2O =$ the common ether; or,

(4) $C_2H_5O \cdot SO_2 \cdot C_2H_5O$ heated strongly $= (HO)_2SO_2 + 2C_2H_4 =$ ethylene. It is to be noted that in both cases the sulphuric acid is regenerated.

630. Methyl alcohol, CH_3OH, may be obtained from the oil of wintergreen, $CH_3 \cdot O \cdot C_7H_5O_2 =$ methyl salicylate, and from crude wood vinegar. Wood-vinegar, obtained by the destructive distillation of wood (Exp. 162), contains about one per cent of methyl alcohol. The crude wood-spirit has an offensive odor and taste, but pure methyl alcohol is a limpid, volatile fluid, very similar in odor and taste to ethyl alcohol.

It has also many of the properties of ethyl alcohol, and is used in the arts for making varnishes and dissolving volatile oils, and in lamps as a convenient source of heat. In England, a mixture of ordinary alcohol with ten per cent of methyl alcohol is sold, free of excise duty, under the name of methylated alcohol, for manufacturing purposes.

631. Ethyl alcohol, $C_2H_5 \cdot OH$ or CH_3CH_2OH, has been prepared synthetically, but the process is time-consuming. It is present in all fermented and distilled liquors, and gives to them their intoxicating properties. Absolute alcohol is a colorless, limpid, easily inflammable liquid, of fiery, pungent taste, and pleasant odor. Sp. gr. 0.79; boiling point, 78°.4C. (173°F). It has recently been solidified by cold of —131°C. It is sometimes used for filling thermometers intended for measuring low temperatures.

Absolute alcohol dissolves potassium and sodium, forming ethylates, like $C_2H_5 \cdot OK$. With chlorine it forms a variety of products: (1) $CH_3CH_2OH + Cl_2 = 2HCl + CH_3CHO =$ *aldehyde,* which is the principal product when weak alcohol is used.

(2) $CH_3CH_2OH + Cl_8 = 5HCl + CCl_3 \cdot CHO =$ *chloral*, which is a product of long-continued action.

(3) And also acts oxidizing when in presence of water; as, $CH_3CH_2OH + H_2O + Cl_4 = 4HCl + CH_3COOH =$ *acetic acid.* Still further, the nascent hydrochloric and acetic acids, liberated by these reactions, produce, with other alcohol molecules,

(4) $C_2H_5OH + HCl = H_2O + C_2H_5Cl =$ *ethyl chloride;* and,

(5) $C_2H_5OH + C_2H_4O_2 = H_2O + C_2H_5 \cdot O \cdot C_2H_3O =$ *ethyl acetate.*

(6) Aldehyde and acetic acid are also produced by the oxidation of alcohol; as, by chromic mixture, etc.

(7) When caustic potash is present the chloral, formed by reaction (2), is converted to potassium formate and *chloroform*,

$$CCl_3 \cdot CHO + KHO = H, COOK + CHCl_3 = \text{chloroform}.$$

Iodine, under like conditions, produces *iodoform*, CHI_3, which is obtainable upon evaporation in yellow scales, and is a valuable test for the presence of alcohol.

Alcohol dissolves many inorganic substances; as, I, KHO, $SrCl_2$, but is especially useful as a solvent for organic compounds, like the alkaloids, essential oils, and the resins; *e. g.*, camphor. It mixes with water in all proportions, causing an elevation in temperature, and a contraction in volume = 51.9 vols. of alcohol + 48.1 vols. of water contracting to 96.5 volumes, producing a mixture which is very nearly $C_2H_5 \cdot OH, 3H_2O$. Accordingly, it readily absorbs water from other substances, coagulating albumin almost instantaneously, and hence acting as an active poison; but like several other poisons also acting as a preservative for animal tissues immersed in it.

632. Decay and fermentation are natural processes which result in the breaking up of complex organic substances into simple compounds. It is generally customary to apply the term "decay" to the putrefaction or rotting of substances containing nitrogen, as albumin. This takes place rapidly in warm, moist air, and ap-

parently spontaneously, producing carbonic anhydride, ammonia, water, and a variety of offensively smelling products which have never been utilized.

Fermentation is applied to the decompositions of non-nitrogenous bodies, yielding of themselves no offensive odors, but producing, besides carbonic anhydride and water, useful products like alcohol and acetic acid. There are several kinds of fermentation which have been named saccharine, vinous, acetic, lactic, etc., after the useful product. Decay and fermentation are supposed to be due to the presence of a third body, called a ferment.

Ferments, so far as known, always contain nitrogen. They are of two kinds: (1) Unorganized soluble bodies, which are undergoing some sort of a change, as the ptyalin of the saliva and the diastase of grain. (2) Organized structures, which are plants or animals actually living and growing, like the yeast-plant.

633. Two theories of fermentation emphasize one or the other of these facts. Liebig believed that when nitrogenous bodies decay, a tremendous disturbance is set up among their molecules, which is capable of inducing similar disturbances among the molecules of carbohydrates, like starch. The molecular change which thereby results is fermentation; the decaying body is a ferment, and is said to act by its presence (catalysis).

Pasteur supposed (1) that everywhere in the atmosphere are "germs" of organized bodies as abundant as the motes in the sunbeam; (2) that when these germs fall into a *nidus* containing their proper food, air, moisture, and a suitable warmth, they grow; (3) by their growth nitrogenous substances pass into decay; non-nitrogenous substances into some sort of fermentation; (4) and that each kind of fermentation is excited most readily by some peculiar microscopic plant or animal.

634. The ferment in vinous fermentation is usually

yeast. Yeast is a monocellular plant which grows at the expense of the nitrogenous matters which are present in the crude fruit juices and malt infusions. The best conditions for its growth are aqueous solutions containing less than 20% of sugar, and a temperature between 25° and 35°C. It grows with great rapidity, often increasing in weight seven fold in as many days. It may be killed by freezing or by boiling, and by the presence of antiseptics. Nevertheless, it may be dried by pressure, and is an article of commerce.

FIG. 102. YEAST-PLANT.

When examined by the microscope, two sets of cells are always found, which has led some to suppose that there are really two yeast-plants. One of large cells (saccharomyces cerevisiæ), which is the top yeast, used in brewing ale and in the mash of "high wines;" the other much smaller (penicillium glaucum), of comparatively slow growth, which is the "bottom yeast" of lager beer. This bottom yeast is supposed also to be an active ferment in butyric and lactic acid fermentation.

635. The glucoses, $C_6H_{12}O_6$, are the only substances which may be made to undergo vinous fermentation. They exist in most ripe fruits, and are easily obtained from cane sugar, or from starch by assimilation of water; cane sugar, $C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$;

starch, $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$; glucose.

The chief products of vinous fermentation are carbonic anhydride and ethylic alcohol, $C_6H_{12}O_6=2CO_2+2C_2H_5OH$, mixed always with small amounts of glycerol and of succinic acid; frequently, also, traces of acetic and lactic acids, and the higher

homologues, propylic, butylic, and amylic alcohols, which are separated in distillation as "fusel-oil." It will also be remembered that wine and other fermented liquors contain the sugar which has escaped fermentation and soluble matters, like tartaric or citric acids derived from the fruit juices, or from the malt extract.

636. Fermented liquors, such as wine and cider, are made from the natural fermentation of the expressed juice or *must* of grapes and apples. On exposure of the juice to the air, the albuminous matters present enter into the state of decay, and a spontaneous fermentation is set up in the fruit sugar. No yeast is added. When the fermentation ceases, the clear wine is drawn off into casks and set in cool cellars to ripen. As the wine becomes stronger in alcohol, a red crust, called *argol*, which is acid potassium tartrate, separates out, and the wine becomes sweeter. The malic and citric acids present in cider and currant juice can not be so withdrawn. The bouquet, or flavor, of these liquors is due to small quantities of ethers, like the acetic and œnanthylic.

Strong wines, like sherry, which do not change to vinegar upon exposure to the air, contain from 15 to 20 per cent of alcohol. The sour wines, like claret and the Rhine wines, contain from 7 to 12 per cent of alcohol, and almost no sugar. In sparkling wines, like champagne, a part of the sugar ferments after the wine is bottled, thereby evolving CO_2.

637. Ale and beer are fermented liquors prepared from malted barley. The operation of malting consists in causing moistened barley to germinate in warm, moist air, for 10 or 15 days. The germ is then killed by drying. It is now malt, and contains most of the starch of the barley, some dextrine and sugar, and a remarkable nitrogenous substance called *diastase*, directly derived from the germ of the plant. This diastase is a soluble ferment, capable of converting 1000 times its weight of starch into glucose, $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$, or ten

times the weight of the starch associated with it in the malt.*

In brewing, the malt is first screened and crushed. It is then *mashed* in large tubs with water, and heated for several hours at 75°C. In this time, the diastase converts nearly all of the starch of the grain into dextrine and malt sugar, which dissolve. The clear liquor strained from the spent barley husks is the *wort*. It has a sweet, insipid taste.

The wort is now boiled in large copper kettles, and a quantity of hops added. The hops give a bitter, aromatic taste to the beer, and perhaps act as a narcotic. By the boiling, the diastase is destroyed, the albuminous matters coagulated, and the wort becomes clarified. The clear liquor is now drawn off, cooled rapidly, and transferred to enormous tubs called the fermenting vats.

At this stage, brewers of ale and of lager beer vary in their methods. Stock ale contains more alcohol, and requires a stronger malt than lager beer; and ale is made from top yeast; lager, from bottom yeast.

The yeast which is now added sets up a vinous fermentation. The process continues for several days (3 to 8), or until nearly three fourths of the glucose has been converted to alcohol and carbonic anhydride,

$$\text{yeast} + C_6H_{12}O_6 = 2CO_2 + 2C_2H_5OH.$$

The clear liquor is now separated from the yeast; the ale is drawn into casks, and the lager into enormous tuns, which are placed in cool, quiet cellars. In both, a slow fermentation continues for some time, consuming sugar, but rendering the beer stronger, besides charging it with the froth-producing carbonic anhydride. In a few days the ale casks are closed by bungs, but it requires several

* Distillers and some brewers take advantage of this property, adding to the barley mash large quantities of other raw grain, rice, or glucose.

months before the lager is fit to be transferred to the kegs in which it is sold. The color of ale and beer is due to caramel, which is produced when malt is roasted. Lager beer contains from one to five per cent of alcohol; the strong ales, as high as ten per cent. These beverages also contain a little unchanged sugar, dextrine, albumin, an extract from the hops, besides traces of acetic, lactic, and succinic acids.

638. Distilled liquors are first fermented and then distilled; as brandy is distilled from wine. Most ardent spirits are made by first malting and mashing barley, as in the process of making ale. The diastase of the malt is employed to convert as large a quantity as possible of rye, corn, rice, crushed potatoes, etc., into glucose. No hops are added, nor is the wort boiled. A large amount of yeast is then added, and the fermentation made as complete as possible to convert all the sugar into alcohol. The "sweet mash," prescribed by excise law, is completed in 48 hours; the "sour mash" requires a longer time, also setting up an acid fermentation by which alcohol is lost, but which is thought to improve the flavor of whiskey.

The fermented mixture is now brought into stills, and subjected to fractional distillation. The first product is thrown back into the still, the next is "high wine," containing from 40 to 70 per cent of alcohol, and then a weaker "low wine," which is reserved for redistillation.

Proof-spirit is a mixture of $49\frac{1}{2}$ parts of alcohol with $50\frac{1}{2}$ parts of water. The high wines are either rectified into cologne spirit and whiskeys by filtering through animal charcoal, which absorbs both the fusel-oil and coloring matters, or they are redistilled into commercial alcohol, containing as high as 92% alcohol.

The strongest commercial alcohol, 98%, is treated also with quick lime, which combines with the water, and is then again distilled. Absolute alcohol, 100%, is made by repeating this process. It should not give a blue tinge to anhydrous cupric sulphate.

639. As regards spirituous liquors, it may be added that gin owes its flavor to juniper berries. Rum is made from molasses, arrack from rice, koumiss from milk. The cordials contain cologne spirits, various essential oils, and sugar.

Most ardent spirits, when first distilled, have a raw, fiery taste, which becomes milder when they are kept for some time in wooden barrels. A portion of the spirit escapes, and with it much of the *bye* products, as aldehyde, fusel-oil, etc., which are replaced by a characteristic flavor or *bouquet.* This bouquet is supposed to be due to the oxidation of the higher alcohols present, and the consequent formation of fragrant fruit ethers. "Compounders of liquors," by the aid of ethers made from the various fusel-oils, have been able to make from cologne spirits any kind of whiskey, brandy, gin, etc., so excellently well as to deceive the best judges. §758.

640. The term "fusel-oil" is given to a variable mixture of several alcohols of high boiling point, which pass over at the end of an ordinary distillation of "spirits." Potato fusel is mainly iso-amyl alcohol. Beet-root fusel is iso-butyl and iso-amyl alcohol. Apple-brandy fusel is propyl alcohol. The fermented marc of grapes contains in its fusel, propyl, hexyl, and octyl alcohols, separable by a careful fractional distillation.

641. Iso-amyl alcohol, which is the ordinary amyl alcohol of fermentation, requires further mention. Especially, because it is a mixture of two isomers, one optically inactive, the other with a right-handed polarization. It does not mix with water, and is a good solvent of many alkaloids, like morphine; hence it has been applied to remove these bodies from aqueous mixtures that contain them.

642. Cetyl alcohol, $C_{16}H_{33}OH$, is a solid, white, tasteless mass, which is obtained by saponifying the spermaceti found in sperm whales.

$$C_{16}H_{33}\cdot O\cdot C_{16}H_{31}O = \text{cetyl palmitate.}$$

Ceryl alcohol is produced from Chinese-wax; and *myricyl* alcohol, from that part of common bees-wax which is insoluble in ethyl alcohol.

643. Allyl alcohol, $C_3H_5OH = C_2H_3CH_2OH$, is the only well known alcohol of its series. It is obtained from glycerin, which is propenyl alcohol, $C_3H_5(OH)_3$, by heating this with one fourth of its weight of oxalic acid. It resembles ethyl alcohol; sp. gr., 0.86; boils at 97°C. It yields on oxidation acrolein, $C_2H_3 \cdot CHO$, an aldehyde, and $C_2H_3 \cdot COOH$, acrylic acid, but mostly formic and acetic acids. It is especially interesting because of its compounds with sulphur, which exist naturally in alliaceous plants and some cruciferæ, and which have also been produced artificially, as oil of garlic, $(C_3H_5)_2S$, a true sulpho-ether, and oil of mustard, $C_3H_5 \cdot S \cdot CN$, a sulpho cyanate. Propargylic alcohol, C_3H_3OH, of the series $C_nH_{2n-3}OH$, is also known. The other monatomic alcohols belong to the benzene and cinnamine series.

644. The glycols are dihydric alcohols of the general formula, $C_nH_{2n}(OH)_2$. They may contain primary (CH_2OH), secondary $(CHOH)$, or tertiary (COH), alcohol groups; *e. g.*, ethene glycol is a double primary, $CH_2OH \cdot CH_2OH$, and pinacone (the isomer of hexyl glycol) is a double tertiary, $(CH_3)_2 \cdot COH \cdot COH \cdot (CH_3)_2$. The chemical transformations of the glycols resemble those of the alcohols so far as they take place in the class radicals, but they are of much greater variety, inasmuch as both hydroxyl groups, or one only, may be replaced by other radicals. The primary glycols, when oxidized, form two series of acids (the lactic and the oxalic), and the other alcoholic derivatives, aldehydes, ethers, etc.

Six glycols are known, colorless, syrupy liquids, soluble in water and in alcohol, which resemble, in mode of formation and properties, ethene glycol.

645. Ethene glycol, $CH_2OH \cdot CH_2OH$, is prepared by (1) heating a mixture of equal parts of ethene di-bromide and an alcoholic solution of potassium acetate for several hours, in stout flasks, securely stoppered,

$$CH_2Br \cdot CH_2Br + 2(KOC_2H_3O) + C_2H_5OH = \\ 2KBr + C_2H_5 \cdot O \cdot C_2H_3O + CH_2OH \cdot CH_2 \cdot O \cdot C_2H_3O;$$

(2) separating out the ethene acetate, and then (3) decomposing it by potassium hydrate and distilling,

$$CH_2OH \cdot CH_2O \cdot C_2H_3O + KHO = \\ KOC_2H_3O + CH_2OH \cdot CH_2OH.$$

Ethene glycol is a colorless, sweetish liquid, of the consistency of a thin syrup, having an odor somewhat like that of ethyl alcohol. Sp. gr., 1.125; boils at 197°C. It is sparingly soluble in ether.

It yields a great variety of substitution products; *e. g.*, it is oxidized by cold nitric acid to

$CH_2OH \cdot CH_2OH + O_2 = H_2O + CH_2OH \cdot COOH =$ *glycollic acid*, which is half alcohol and half acid, and by heated nitric acid to $CH_2OH \cdot CH_2OH + O_4 = 2H_2O + COOH \cdot COOH =$ *oxalic acid.* It forms compound ethers with the alcohol radicals; as,

$$CH_2OH \cdot CH_2O \cdot C_2H_5 = \text{ethylic ethenate};$$

ethereal salts, with acid radicals; as,

$$CH_2OH \cdot CH_2O \cdot C_2H_3O = \text{ethene acetate};$$

and a peculiar variety of simple ethers, called poly-ethenic alcohols, by abstraction of water and condensation of two or more molecules; as, $2(C_2H_4(OH)_2) - H_2O = C_2H_4OH \cdot O \cdot C_2H_4OH$.

646. Two tri-hydric alcohols, or *glycerols*, are known, of the general formula $(C_nH_{2n-1})'''(OH)_3$. The only one of importance is usually called

GLYCERIN, $C_3H_8O_3 = CH_2OH \cdot CHOH \cdot CH_2OH$,

which may be obtained from most of the fixed oils and fats by saponification. These substances are ethereal salts containing the trivalent propenyl, C_3H_5, and three

monovalent acid radicals belonging to the fatty and the oleic series. Mutton-suet is largely tri-stearin (a solid), $C_3H_5 \vdots O_3 \vdots (C_{18}H_{35}O)_3$; palm-oil is nearly tri-palmitin, $C_3H_5 \vdots O_3 \vdots (C_{16}H_{31}O)_3$; and olive-oil is principally triolein, $C_3H_5 \vdots O_3 \vdots (C_{18}H_{33}O)_3$.

The ordinary fatty substances contain mixtures of these and their homologues. All of them decompose when boiled with strong bases. The acids unite with such bases to form a soap, and glycerol is liberated. The usual process consists in decomposing such fats by superheated steam; as,

$$C_3H_5 \equiv O \equiv (C_{18}H_{35}O)_3 + 3H_2O = 3(C_{18}H_{35}O \cdot OH) + C_3H_5(OH)_3.$$

Pure glycerol is a sweet, viscid liquid, which boils at 290°C, and solidifies at very low temperatures. When strongly heated, it decomposes into $2H_2O$ and *acrolein*, an aldehyde causing the irritating odor noticed when grease is dropped on a hot stove. Glycerol has considerable solvent powers, does not easily oxidize nor evaporate,—qualities which render it valuable to pharmacists.

647. Glycerol may be oxidized to glyceric acid,

$$CH_2OH \cdot CHOH \cdot COOH,$$

but is usually decomposed by oxidizing agents to formic and oxalic acids.

It may give rise to three series of substitution products according as one, two, or three hydroxyl groups are replaced by other radicals. The ethers so formed have names ending in "*in*." For example, HCl converts it first to mono-chlorhydrin, $C_3H_5(OH)_2Cl$, then to dichlorhydrin, $C_3H_5OHCl_2$; finally PCl_5 forms with this tri-chlorhydrin, $C_3H_5Cl_3$. Fuming nitric acid produces with it *tri-nitro-glycerin*, $C_3H_5 \cdot O_3 \cdot (NO_2)_3$, a heavy, oily liquid, which burns quietly when inflamed by a lighted fuse, but which explodes with fearful violence by percussion. It is a constituent of dynamite and other explosives.

When glycerol is heated in sealed tubes with acids, it yields ethereal salts, which are called *glycerides;* thus, there are three acetins;

$$\text{Mono-acetin, } (C_3H_5)(OH)_2 \cdot O \cdot C_2H_3O;$$
$$\text{Di-acetin, } (C_3H_5)(OH) : O_2 : (C_2H_3O)_2;$$
$$\text{Tri-acetin, } (C_3H_5) \vdots O_3 \vdots (C_2H_3O)_3.$$

In this way, the stearin, palmitin, and olein of natural fats have been produced artificially.

648. Erythrite, $C_4H_6(OH)_4$, the only tetrahydric alcohol known, exists in erythrin, a constituent of several coloring matters. It forms colorless, sweet-tasting crystals.

649. Mannite, $O_6H_8(OH)_6$, and its isomer, *dulcite*, are hexahydric alcohols, and are sugars found naturally in certain plants.

Mannite is obtained in needle-like crystals, not fermentable, from the dried sap of the manna ash. It may also be produced artificially from glucose by nascent hydrogen, $C_6H_{12}O_6+H_2=C_6H_{14}O_6$.

The structural formulæ following show its oxydation by two stages to mannitic and saccharic acids:

$$\text{Mannite, . . . } \begin{array}{l} CHOH \cdot CHOH \cdot CH_2OH, \\ | \\ CHOH \cdot CHOH \cdot CH_2OH. \end{array}$$

$$\text{Mannitic acid, . . } \begin{array}{l} CHOH \cdot CHOH \cdot CH_2OH, \\ | \\ CHOH \cdot CHOH \cdot COOH. \end{array}$$

$$\text{Saccharic acid, . . } \begin{array}{l} CHOH \cdot CHOH \cdot COOH, \\ | \\ CHOH \cdot CHOH \cdot COOH. \end{array}$$

Dulcite oxidizes to *mucic* acid, which is isomeric with saccharic acid. These two acids are generally obtainable by the oxidation of the various carbohydrates with nitric acid.

Recapitulation.

The alcohols are found in three metameric forms, containing CH_2OH (primary), CHOH (secondary), and COH (tertiary), radicals.

In each of these forms, true isomers are possible, as in the case of amyl alcohol.

The primary alcohols oxidize first to aldehydes, then to acids.

The secondary alcohols oxidize to ketones.

The tertiary alcohols break up upon oxidation, forming two acids of lower carbon content.

Alcohols are also grouped according to the number of hydroxyl radicals they contain: the carbinols, one OH; the glycols, two OH; the glycerols, three OH, etc. Also, with reference to their alkyl radical; as, C_nH_{2n+1} (methyl series); C_nH_{2n-1} (allyl series), etc.

The ordinary alcohol is *ethylic*, found in fermented liquors, like ale, beer, and wine; in ardent spirits, like whiskey; in high wines, and pure in absolute alcohol.

Two theories of fermentation are presented: Pasteur's, which supposes the presence of living plants and animals; Liebig's, which is based upon molecular disturbances; and two sets of ferments are recognized, the soluble and the organized.

CHAPTER XXI.

THE CARBOHYDRATES.

650. The carbohydrates, $C_y(H_2O)_x$, are widely distributed in the vegetable world, and play a most important part in the life of a plant, which forms starches, sugars, or gums, according to its apparent needs.

They form, naturally, numerous isomers, which yield to the chemist products so intimately related as to indicate a close relationship. Their aqueous solutions are generally optically active. Most turn the plane of polarization to the right (dextrose), but not to the same extent; a few, as lævulose and inulin, strongly to the left. They are neutral bodies, containing both alcoholic (CH_2OH or CHOH) and aldehydic radicals (HCO), and are, therefore, readily oxidized. When oxidized with nitric acid, all yield, as a final product, oxalic acid; but, in the intermediate stages, saccharic or mucic acids, and frequently also formic acid. It must be noted that they do not contain *water as such,* although they contain H and O in the proportion $(H_2O)_x$.

651. The carbohydrates from three groups. I GROUP. The glucoses, $C_6H_{12}O_6$, are alcoholic aldehydes,

$$CH_2OH(CHOH)_4CH:O.$$

They include mannitose, dextrose, lævulose, maltose, lactose;—all of which, in contact with yeast, pass into vinous fermentation, and several others little known, not fermentable; as, inosite (existing in muscular flesh), and sorbin (from mountain ash berries).

II GROUP. Saccharoses, $C_{12}H_{22}O_{11}$, have not been obtained artificially, and are not fermentable. On long boiling with dilute sulphuric acid, they suffer "*inversion,*"

absorbing a molecule of water, and forming a mixture of the two fermentable glucoses; as,

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}.$$

They may, therefore, be regarded as anhydrides of di-glucose. They include cane sugar, malt sugar, milk sugar, and less important isomers.

III GROUP. Amyloses $(C_6H_{10}O_5)_x$, are tasteless bodies, which are converted into the glucoses by diastase or by boiling with sulphuric acid, acting in this respect as anhydrides of the sugars. Their molecular weight is thought to be double or treble that of their empirical formulæ. They form several sub-groups: cellulose and tunicin; starch, inulin, and glycogen; dextrin; gum and mucilage, and pectin.

652. Cellulose, $3C_6H_{10}O_5$, forms a large proportion of the solid parts of plants. It is well represented by purified vegetable fiber, such as filter paper. Pure cellulose is white, translucent, insoluble in water, alcohol, and ether, not acted upon by dilute acids, nor by alkalies, and is quite innutritious. It dissolves in an ammoniacal solution of basic cupric carbonate, from which it is precipitated in white flakes by acids. Cellulose is not colored by iodine.

Transformations. In cold, concentrated sulphuric acid, cellulose is converted to a jelly-like mass, which, if thrown into a large quantity of water, deposits white flakes of an isomer, called *amyloid*, because it is colored blue by iodine. By a longer contact with the strong acid, the cellulose changes to a second isomer, dextrin; finally, upon boiling the solution, the dextrin assimilates water and changes to glucose.

If unsized paper be dipped for a few seconds in a cold mixture of two volumes of strong H_2SO_4, and one volume

of H_2O, the surface becomes converted to amyloid. If the paper be now thoroughly washed, it will be found to have become tougher, and is not softened by water. It is sold as a substitute for parchment, under the name of parchment paper.

653. The cellulo-nitrins are made by steeping finely-divided cellulose in a mixture of nitric and sulphuric acids, and subsequently washing and drying the products, which have increased in weight without undergoing any change in external appearance. Several nitryl (NO_2) substitution products may be formed, depending partly on the strength of the acids, and partly on the time consumed.

With two parts of the strongest nitric and one of sulphuric acid, tri-nitrocellulose forms, $C_6H_7O_5(NO_2)_3$. This is gun-cotton or pyroxylin, four-fold as explosive as gunpowder, employed to some extent in the Austrian service, and in blasting. It is insoluble in alcohol and ether. Less highly nitrated compounds are less explosive, but are soluble in a mixture of ether and alcohol, producing *collodion*. This solution of collodion evaporates speedily, leaving a transparent, flexible, and adhesive film, which is largely used in making photographic negatives on glass.

Tunicin is animal cellulose, occurring in the mantle of ascidians.

654. Starch, $(C_6H_{10}O_5)_3$, is found in the cells of all growing plants, most abundantly in certain seeds (cereal grains, rice, chestnuts), in soft stems (sago-palm), in roots (arrow-root and tapioca), and in tubers (potato). It is prepared by reducing the vegetable structure to a pulp, and washing with much cold water upon a fine sieve. The cellular tissue remains behind, the starch passes through with the water and soon settles as a white sediment. It is then washed and dried at about

140°F; but still retains considerable hygroscopic water (10 to 18%), and small quantities of wax and fat.

When the various sorts of starch are examined under the microscope, they are found to consist of minute ovoid granules, which appear to be made up of concentric layers, covered with an exceedingly delicate envelope of cellulose. The granules from different plants vary in size and shape, those from the potato having four times the diameter of those from wheat and rice. See Fig. 103.

FIG. 103.

When heated in a little water above 60°C., the envelopes burst, and the starch appears to dissolve, but, on cooling, it settles to a jelly-like mass (starch paste), which may be dried to a hard, transparent mass. After long boiling, starch no longer gelatinizes, but is converted to *soluble starch.* All forms of starch are characterized by forming, with traces of iodine, a beautiful blue color. When starch is boiled in water containing diastase, or a very small amount of sulphuric acid, it changes first to *soluble starch*, then to dextrine, and finally to dextrose. It is oxidized by nitric acid to saccharic and oxalic acids, and forms, with concentrated nitric acid, xyloidin, $C_6H_9NO_2O_5$, an inflammable body, resembling gun-cotton.

The uses of starch in the laundry are well known. Raw starch is digested with difficulty; on the other hand, cooked starch is very wholesome, and is an important article of food.

655. Bread-making. Wheat flour contains about 60% of starch, 10% of dextrine and sugar, and 10% of a nitrogenous substance called *gluten.* When flour is mixed with about half its weight of water, it forms a *dough*, which is tenacious in proportion to the gluten it contains. This dough baked is unleavened bread, unpalatable and difficult of digestion. But if the dough be dis-

tended by carbonic anhydride, it forms a porous sponge, which (after kneading to render the cavities of uniform size) is baked at a temperature sufficient to burst the starch granules, and convert a portion of them to dextrin, and becomes *bread.*

The carbonic anhydride necessary for "aërating" the sponge is obtained in many ways; the oldest by means of vinous fermentation set up, primarily, in the sugar of the flour, and afterwards in the starch by putrefaction of old dough or leaven, or by warm mixtures of salt and water; and, secondly, by yeast, whose action has already been described; thirdly, obtained from the decomposition of an alkaline bicarbonate by some acid or acid salt, such as the lactic acid of sour milk, tartaric acid, cream of tartar, super-phosphate of lime, etc.; *baking powders* are mixtures of this sort. Bicarbonate of ammonia is sometimes used alone by cake-bakers. Fourthly, by forcing the gas or air through the dough by mechanical contrivances, "aërated bread." On baking, the carbonic acid and alcohol, which have formed, are driven off. Good bread contains about 40% of water. The apparent drying of stale bread does not consist wholly in loss of water, but also in an internal change in the particles of the bread. A stale loaf gently heated in a closed vessel for an hour regains the properties of new bread.

656. Iceland moss, inulin, and glycogen are starch-like substances, which are not colored blue by iodine. Inulin obtained from dahlia tubers and roots of the dandelion, changes by boiling with dilute acids into pure lævulose. Glycogen, an animal starch found in the liver of several animals, changes with great rapidity into dextrose by the action of saliva.

657. Dextrin, $C_6H_{10}O_5$, is formed from starch by the action of diastase, and also by boiling with dilute acids. It is best manufactured by moistening starch with water

containing 2% of nitric acid, drying and finally roasting to 110°. Dextrin is a yellowish powder, freely soluble in water, and not changed blue by iodine. Its solution turns the plane of polarization strongly to the right, whence its name.

It is the gum used on postage stamps, under the name of "British gum." It is extensively used in calico printing for thickening mordants instead of the true gums.

658. The gums are mixtures of amorphous brittle bodies, the dried exudation from many plants. The best known are from the acacias; viz., gum arabic and gum senegal. These contain from 70 to 80 per cent of *arabin*, $C_{12}H_{22}O_{11}$, soluble in water, but changing on being heated to 130°C. to metarabin $(C_6H_{10}O_5)_x$, which swells up to a jelly-like mass in water, but does not dissolve. Arabin and metarabin are common in plants, as in the exudations from cherry and plum trees.

Bassorin is found frequently mixed with arabin, as in peach-tree gum. It forms with water a gelatinous mass, which is a mucilage. It is the principal constituent of Gum Tragacanth. Other mucilages, as those found in mallows and linseed, are isomers of starch, but are soluble in water.

659. Pectose and pectin are found widely distributed in plants. Pectose (which is insoluble in water) in unripe, fleshy fruits and roots, is converted by fermentation to pectin, a soluble substance which is found in ripe fruits, and which gives to their juices the property of gelatinizing when boiled (currant jelly). It readily changes to other gelatinous bodies, and finally to metapectic acid, which is very nearly arabin.

660. Glucose, or grape-sugar, is found in most ripe sweet fruits. It generally contains two isomers, dextrose and lævulose, which differ principally in the fact

that solutions of dextrose turn the plane of polarized light to the right (+56°), and of lævulose to the left (—104°). Inverted sugar is a mixture of equal molecules of both, found naturally in honey, and produced from cane sugar by ferments, by boiling, etc.

Dextrose (ordinary glucose), $C_6H_{12}O_6$, is found in diabetic urine. As already noted (p. 327) it is produced in germinating seeds by the action of diastase upon starch. It is prepared in large quantities by boiling starch with dilute sulphuric acid,

$$\text{starch, } C_6H_{10}O_5 + H_2O = C_6H_{12}O_6\text{, glucose.}$$

After some hours, chalk is added to neutralize the acid, and the solution is drawn off. On concentrating the liquid to a syrup, the dextrose crystallizes in cauliflower-like masses.

Glucose dissolves in 1.2 parts of cold water. It is less sweet than invert sugar, and much less than cane sugar.

Like other aldehydes, the glucoses are strong reducing agents, especially when warmed, reducing the noble metals easily—bismuth, copper, etc., in alkaline solutions. Fehling's solution, containing cupric tartrate, dissolved in caustic alkali, is an excellent test for glucose, producing the red cuprous oxide, Cu_2O, on heating, § 468. Cane sugar does not produce this reaction until it has suffered inversion. On oxidizing, the glucoses are changed to saccharic acid.

Lævulose, $C_6H_{12}O_6$, or fruit sugar, $C_6H_{12}O_6$, H_2O, may be obtained pure from inulin by the same methods that dextrose is obtained from starch. Also by treating invert sugar with milk of lime, which forms an insoluble lime salt with lævulose, and not with dextrose.

Lævulose exhibits the same chemical characters as dextrose, but is less easily fermented. Most of their products are identical. When heated to about 170°C., dextrose and lævulose each lose a molecule of water, and form *glucosan* and *lævulosan*, $C_6H_{10}O_5$. These are obtained from cane sugar also. On heating any sugar

to about 200°C. a brown mixture, called *caramel*, is produced, but at higher temperatures the sugars are completely decomposed. Mannitose is optically inactive, but in other respects resembles lævulose.

661. The glucosides are substances widely distributed in the vegetable world, which so far resemble the ethereal salts that they are resolved by boiling with dilute acids, as also by contact with ferments into some sort of sugar, which is generally glucose, and to other compounds. For example, amygdalin, $C_{20}H_{27}NO_{11}$, found in the kernels of bitter almonds, peaches, etc., by boiling with dilute HCl, assimilates H_2O, and forms glucose, prussic acid, and the oil of bitter almonds; thus,

$$C_{20}H_{27}NO_{11}+H_2O=2(C_6H_{12}O_6)+HCN+C_6H_5CHO.$$

The same change takes place when the juice of crushed almonds is exposed to the air, by reason of a natural ferment, *emulsin*, which is also contained in the almond. Among the most important of the glucosides are *indican* and *ruberythric acid* (the sources of indigo and madder); valuable medicinal agents, like jalapine and digitaline; and poisons, like solanine and antiarine.

662. Lactose, $C_6H_{12}O_6$, is obtained by inversion of milk sugar. It contains two sugars, one of which resembles dextrose, producing saccharic acid on oxidation; the other yielding mucic acid. Both are fermentable, and reduce Fehling's solution.

663. Saccharose, $C_{12}H_{22}O_{11}$, or cane sugar, is found to some extent in the juices of nearly all plants; very abundantly in sorghum, maple sap, beet-roots, and the sugar-cane. It is prepared from the crude juices of such plants by (1) neutralizing with 0.5% of milk of lime to prevent inversion; (2) boiling to coagulate albuminous substances; (3) filtering through thick layers of animal charcoal to remove these and the coloring matters;

(4) evaporating *in vacuo* as rapidly and at as low a temperature as possible. (5) When the solution has become sufficiently concentrated to crystallize on cooling, it is drawn into pans and stirred, so as to promote the formation of a *granulated* sugar. (6) This raw sugar is finally drained from a portion that is not crystallizable, and which is *molasses.* Raw sugar is refined by a second or third treatment with bone black, forming white sugar and residues of syrups.

Cane sugar is soluble in $\frac{1}{3}$ of its weight of cold water. It may be obtained from its solution by slow evaporation in large monoclinic prisms (rock candy). When heated to 160°C it melts, and, on cooling, forms an amorphous transparent mass (lemon candy).

Cane sugar is at once decomposed by strong sulphuric acid, evolving much SO_2, and formic acid, $H \cdot COOH$, and blackening from separation of carbon (distinction from glucose). Distilled with MnO_2 and H_2SO_4 it yields formic acid more abundantly. It is interesting to note that glucose is a polymer of formic aldehyde, CH_2O.

664. Milk sugar, $C_{12}H_{22}O_{11} + H_2O$, is found only in the milk of animals. When the whey of milk is evaporated to a syrup, and allowed to stand for some time, the sugar of milk forms in crusts. It is soluble in six parts of cold water, and is harder and less sweet than cane sugar.

It resembles cane sugar in most chemical reactions, reducing silver and copper salts slowly, and is resolvable into fermentable sugars. These *lactoses* yield, on fermentation with cheese, both alcohol and lactic acid. The Kalmucks prepare an intoxicating drink, called *koumiss,* from the milk of mares.

Maltose, isomeric with milk sugar, is found in malt extract, as an intermediate stage in the conversion of starch to glucose.

Recapitulation.

(1) The carbohydrates, the starches, the true gums, and cellulose, and the various sorts of sugar, are among the natural products of most plants.

(2) The structural formulæ of none of them are certainly known.

(3) Upon oxidation they all yield oxalic acid, with various intermediate products, like mucic and saccharic acids.

(4) Optically, they are mostly dextrogyrate; a few are lævogyrate.

(5) The starches, gums, and cellulose are tasteless. Mannite is sweetish, glucose rather sweet, and the saccharoses "sweet as sugar."

(6) Those that act reducing, resemble the aldehydes; *e. g.*, glucose. Those that resemble mannite are alcohols. Most are aldehydic alcohols.

(7) All seem to contain the six carbon group, with varying amounts of $H \cdot O \cdot H$.

(8) The numerous isomers of the glucoses are, perhaps, polymers of formic aldehyde, $H \cdot CH : O$.

(9) The starches, gums, mucilages, cellulose, and pectin are metamers $(C_6H_{10}O_5)$.

(10) In beer-making, the starch is changed to glucose, this to alcohol and carbonic anhydride.

(11) In ardent spirits, the alcohol is produced from fermented marc or is distilled from mash.

(12) In bread-making, the other product of fermentation, CO_2, is utilized to distend the gluten of the flour.

(13) The baking powders obtain the CO_2 by decomposing $NaHCO_3$ by acids, or by acid salts.

CHAPTER XXII.

ALDEHYDES AND KETONES.

665. These compounds are derived from the alcohols by oxidation. When a primary alcohol is treated with chromic mixture, it is oxidized in two stages.

(1) H_2 is removed from the CH_2OH group, the hydroxyl is broken up, and the product formed is an *aldehyde;* as, $CH_3CH_2OH + O = CH_3, H \cdot CO + H_2O$.

(2) The aldehydes oxidize very readily to *acids*, in which the hydroxyl group is restored; as,

$$CH_3, H \cdot CO + O = CH_3 \cdot COOH.$$

(3) If an alkaline salt of such an acid is strongly heated, a *ketone* is formed,

$$(CH_3COONa)_2 = Na_2CO_3 + CH_3 \cdot CO \cdot CH_3.$$

(4) The ketones are also produced by the direct oxidation of the secondary alcohols; H_2 being eliminated from the CHOH group.

These aldehydes, acids, and ketones contain at least one alkyl radical, C_nH_{2n+1}, etc., united by carbonyl, CO, to some other radical; as, H, OH, or CH_3. Their relationship will be clearly seen by inspection of these formulæ:

CH_3	CH_3	CH_3	CH_3	CH_3
$\vert$	$\vert$	$\vert$	$\vert$	$\vert$
CH_2	$C=O$	$C=O$	$C=O$	$CHOH$
$\vert$	$\vert$	$\vert$	$\vert$	$\vert$
OH	H	OH	CH_3	CH_3
Ethyl alcohol.	Acetic aldehyde.	Acetic acid.	Acetone.	Secondary propyl alcohol.
C_2H_6O	C_2H_4O	$C_2H_4O_2$	C_3H_6O	C_3H_8O.

666. Nascent hydrogen, evolved from sodium amalgam and water, reverses these reactions, converting:

(1) Acid anhydrides or chlorides to aldehydes; as,

$$CH_3 \cdot COCl + H_2 = HCl + CH_3 \cdot COH;$$

(2) the aldehydes to primary alcohols,

$$CH_3COH + H_2 = CH_3 \cdot CH_2OH;$$

(3) the ketones to secondary alcohols,

$$CH_3 \cdot CO \cdot CH_3 + H_2 = CH_3 \cdot CHOH \cdot CH_3.$$

The last reaction affords a general method for preparing the secondary alcohols, inasmuch as a ketone, containing two different alcohol radicals, can first be made by distilling a dry mixture of sodium or calcium salts of two different fatty acids; as,

(1) $CH_3 \cdot COONa$, sodium acetate $+ C_3H_7COONa$, sodium butyrate $=$ $NaO \cdot CO \cdot NaO$, sodium carbonate $+ CH_3 \cdot CO \cdot C_3H_7 =$ methyl propyl ketone.

(2) $CH_3 \cdot CO \cdot C_3H_7 + H_2 = CH_3 \cdot CHOH \cdot C_3H_7 =$ secondary propyl alcohol.

An important exception is found when one of the salts so distilled is an alkaline formate. In such a case an aldehyde will be produced; as,

$$CH_3 \cdot COONa + H \cdot COONa = Na_2CO_3 + CH_3 \cdot CO \cdot H.$$

667. The aldehydes are colorless, volatile liquids of pungent odor. Some of the essential oils are natural aldehydes, as the oils of meadow sweet (spirea), anise, and bitter almonds. Those of the same series strongly resemble each other, but exhibit the usual gradational characters of homologous compounds.

All aldehydes form crystalline compounds with the acid sulphites of the alkalies, easily decomposed by dilute sulphuric acid with the liberation of pure aldehyde. This reaction serves both as a test for the presence of an aldehyde, and also as a means for purifying it. When heated with caustic potash, the aldehydes are converted to a hard mass, called "aldehyde resin."

668. Formic aldehyde, $H \cdot CH:O$, is a gas, obtainable in solution by carefully oxidizing methyl alcohol. Very probably it is produced in the living plant by the action of chlorophyl in the sunlight upon carbonic anhydride and water, $CO_2 + H_2O = \widehat{O}_2 + H \cdot CH:O$. It polymerizes readily, and it is an interesting problem whether some of the numerous polymeric compounds mentioned on page 294 are not derived from this source, and that starch, cellulose, etc., are their condensation products.

Acetic aldehyde, $CH_3CH:O$, is formed by oxidizing ethyl alcohol with chromic mixture and distilling.

It is a colorless liquid, with a pungent, ethereal odor, which mixes with water and alcohol in all proportions; sp. gr. 0.8; boils 21°C. It oxidizes readily to acetic acid, reduces silver from an ammoniacal solution of silver nitrate, the silver depositing on the sides of the vessel in a mirror-like film.

All aldehydes exhibit the characteristics of unsaturated compounds. (1) They readily oxidize to acids having the same number of carbon atoms, and hence are good reducing agents. (2) They show a marked tendency to polymerize, especially when not perfectly pure; thus, acetic aldehyde has two polymers, called para- and meta-aldehydes, each containing two or more molecules, and reconvertible to ordinary aldehyde by heating. (3) They also form condensation products. In the presence of HCl and water, acetic aldehyde gradually changes to aldol, $C_4H_8O_2$.

Aldol is converted to butylene glycol by the action of sodium amalgam, and to oxy-butyric acid by moist silver oxide. It is consequently the aldehyde of the latter. Moreover, on being heated, it loses a molecule of water and condenses further to crotonic aldehyde; thus,

CH_3	CH_3	CH_3	CH_3
|	|	|	|
$CH:O$	$CHOH$	$CHOH$	CH
	|	|	‖
CH_3	CH_2	CH_2	CH
|	|	|	|
$CH:O$	CH_2OH	$CH:O$	$CH:O$
Acetic aldehyde.	Butylene glycol.	Aldol.	Crotonic aldehyde.

669. The chlorine derivatives from aldehydes in mixtures of alcohol, acids, etc., are exceedingly numerous, and involve both radicals, CH_3 and $CH:O$. Dry chlorine gas produces, from acetic aldehyde, acetyl chloride, $CH_3 \cdot CO \cdot Cl$. The action of chlorine upon absolute alcohol has been detailed on page 323. The tri-chlor-aldehyde which forms is *chloral*, $CCl_3 \cdot CHO$, a volatile liquid of penetrating odor; sp. gr. 1.5; boils at 94°C. It changes, on standing, to a porcelain-like modification, *para-chloral*, probably tri-chloral, which distills at 180°, becoming reconverted to chloral. It is an aldehyde, oxidizing to tri-chlor acetic acid, CCl_3COOH. Unlike the other aldehydes, it combines eagerly with water, forming *chloral hydrate*, $CCl_3 \cdot CH(OH)_2$, which forms large crystals, easily soluble in water. Chloral and its derivatives are easily decomposed by alkalies into chloroform and a formate,

$$CCl_3 \cdot CHO + KHO = CHCl_3 + H \cdot COOK.$$

It is similarly decomposed by the alkalies of the blood when administered as a medicine, and produces deep sleep, but not insensibility to acute pain.

The higher aldehydes of this series have numerous isomeric modifications, like the alcohols. The most important will be sufficiently given in connection with their related compounds.

670. Only two aldehydes of the next series, $C_nH_{n-1}CHO$, are known.

Acroleïn is acrylic aldehyde, $CH_2:CH \cdot CHO$, best prepared by heating glycerol with a dehydrating agent, like P_2O_5. It is always produced when a glyceride (a fat) is subjected to destructive distillation.

Pure acroleïn is a volatile liquid boiling at 52°C, and evolving vapors, which are exceedingly irritating. It rapidly oxidizes to acrylic acid. Nascent hydrogen converts it first to allyl alcohol, and then to propyl alcohol.

(*a*) $CH_2:CH\cdot CH:O + H_2 = CH_2:CH\cdot CH_2OH.$
Acroleïn. Allyl alcohol.

(*b*) $CH_2 : CH\cdot CH_2OH + H_2 = CH_3\cdot CH_2\cdot CH_2OH.$
Allyl alcohol. Propyl alcohol.

Furfurol, $C_4H_3O\cdot CH:O$, is formed by heating sugar, bran, etc., with dilute sulphuric acid. It is a colorless liquid, with an agreeable odor, like the oil of cassia. It may be converted to pyromucic acid by oxidation, and to furfuryl alcohol, $C_4H_3O\cdot CH_2OH$, by nascent hydrogen.

671. Only a few aldehydes of the dihydric alcohols are known; theoretically, they are capable of yielding three series.

Glycol on oxidation should yield the following compounds, but the first is unknown:

	I.	II.	III.	IV.
CH_2OH	COH	COH	COH	$COOH.$
|	|	|	|	|
CH_2OH	CH_2OH	COH	$COOH$	$COOH.$
Glycol.	Glycollic aldehyde.	Glyoxal.	Glyoxalic acid.	Oxalic acid.

Glyoxal and glyoxalic acid are easiest obtained by oxidizing ethyl alcohol with nitric acid. Glycollic and oxalic acids are formed by the same reaction.

On neutralizing this mixture with chalk, the calcium salts are formed. The oxalate, being insoluble, is left behind on filtration. Alcohol precipitates the glycollate and glyoxalate, and glyoxal remains in solution.

Glyoxal is a deliquescent solid, easily soluble in alcohol and water. It is a double aldehyde, having the general character of acetic aldehyde, reducing silver oxide, forming two aldehyde ammonias, glyoxaline, $C_3H_4N_2$, and glycosine, $C_6H_6N_4$.

Glyoxallic acid is half aldehyde and half acid. As an aldehyde, it acts reducing, and can be oxidized to oxalic acid. It may be converted by nascent hydrogen to glycolic acid:

$$COH \cdot COOH + H_2 = CH_2OH \cdot COOH.$$

672. The ketones are colorless liquids of a pleasant odor. Their boiling points and specific gravities increase somewhat irregularly with their increase in carbon atoms. The number of ketones possible by theory is enormous, as any monovalent alkyl radical may be united by CO to any other, either alike or different, and thus constitute a ketone. The ketones are metameric with the oxides of the glycols, and also with those aldehydes which contain the same number of carbon atoms; as, (1) propylene oxide,

$$\begin{array}{l} CH_3 \cdot CH \\ \qquad | \quad > O; \text{ and} \\ \qquad CH_2 \end{array}$$

(2) acetone, $CH_3 \cdot CO \cdot CH_3$, are metameric, with propionic aldehyde, $C_2H_5 \cdot CO \cdot H$. Those ketones which contain the methyl group, CH_3, resemble the aldehydes in forming crystalline compounds with potassium bi-sulphite. The ketones are more stable than the aldehydes, being oxidized with difficulty by chromic mixture, and then completely breaking up, yielding two acids, each containing fewer carbon atoms than the ketone. Acetone yields formic and acetic acids:

$$CH_3 \cdot CO \cdot CH_3 + O_3 = H, COOH + CH_3, COOH.$$

They do not act reducing upon an ammoniacal silver solution. Only about thirty ketones have been thoroughly investigated. The first, from which they derive their names, is acetone.

673. Acetone, $(CH_3)_2CO$, best prepared by the destructive distillation of calcium or lead acetate. It is formed also by the dry distillation of citrates, tartrates, sugar, starch, and wood, and on the large scale as a *bye* product from the acetic acid and iron used in preparation of aniline.

Acetone is a clear liquid of peculiar, pleasant odor, soluble in water and alcohol; sp. gr., 0.79; boils at 55°C. It is inflammable, and burns with a smokeless flame.

Nascent hydrogen converts it to isopropyl alcohol and to pinacone, $(CH_3)_2CHO \cdot CHO(CH_3)_2$.

674. Chlorine gas displaces the hydrogen atom for atom in successive stages, and forms six "chlor-acetones," which are colorless fluids of strong odors. There are also numerous other derivatives of acetone. Among these are condensation products obtained by removal of water from two or more molecules; as,

$$3C_3H_6O - 3H_2O = C_9H_{12} = \text{mesitylene},$$

a body belonging to the benzene series.

Methyl-nonyl ketone, $CH_3 \cdot CO \cdot C_9H_{19}$, which may be formed artificially, is the chief constitutent of the oil of rue.

Recapitulation.

(1) Numerous aldehydes and ketones are metameric, both containing alkyl radicals united to carbonyl.

(2) The aldehydes may be reduced to primary alcohols, or oxidized to acids of the same number of carbon atoms.

(3) The ketones may be reduced to secondary alcohols, or oxidized to two acids of less number of carbon atoms.

(4) The aldehydes form compounds with ammonia and aniline, easily crystallizable; the ketones do not.

(5) The ketones are more stable than the aldehydes, and are capable of forming a larger number of isomeric compounds.

TABLE TO EXHIBIT THE POSITION OF THE PRINCIPAL ACIDS IN THEIR SERIES.

ALCOHOLS.	FATTY ACIDS.	OLEIC SERIES.	LACTIC SERIES.	OXALIC SERIES.	MALIC SERIES.	TARTARIC.	CITRIC.
$C_nH_{2n+2}O$.	$C_nH_{2n}O_2$.	$C_nH_{2n-2}O_2$.	$C_nH_{2n}O_3$.	$C_nH_{2n-2}O_4$.	$C_nH_{2n-2}O_5$.	$C_nH_{2n-2}O_6$.	$C_nH_{2n-4}O_7$.
Methyl,	Formic,	. . .	Carbonic,	. . .	. . .	. . .	. . .
CH_4O.	CH_2O_2.	. . .	CH_2O_3.	. . .	. . .	. . .	. . .
Ethyl,	Acetic,	. . .	Glycollic,	Oxalic,	. . .	. . .	. . .
C_2H_6O.	$C_2H_4O_2$.	. . .	$C_2H_4O_3$.	$C_2H_2O_4$.	. . .	. . .	. . .
Propyl,	Propionic,	Acrylic,	Lactic,	Malonic,	Tartronic,	[Mesoxalic],	. . .
C_3H_8O.	$C_3H_6O_2$.	$C_3H_4O_2$.	$C_3H_6O_3$.	$C_3H_4O_4$.	$C_3H_4O_5$.	[$C_3H_4O_6$.]	. . .
Butyl,	Butyric,	Crotonic,	Oxy-butyric,	Succinic,	Malic,	Tartaric,	. . .
$C_4H_{10}O$.	$C_4H_8O_2$.	$C_4H_6O_2$.	$C_4H_8O_3$.	$C_4H_6O_4$.	$C_4H_6O_5$.	$C_4H_6O_6$.	$C_4H_4O_7$.
Amyl,	Valeric,	Angelic,	Oxy-Valeric,	Pyrotartaric,	Oxy-pyrotartaric.	Homotartaric,	. . .
$C_5H_{12}O$.	$C_5H_{10}O_2$.	$C_5H_8O_2$.	$C_5H_{10}O_3$.	$C_5H_8O_4$.	$C_5H_8O_5$.	$C_5H_8O_6$.	. . .
Hexyl,	Caproic,	Pyroterbic,	Leucic,	Adipic,	Adipomalic,	. . .	Citric,
$C_6H_{14}O$.	$C_6H_{12}O_2$.	$C_6H_{10}O_2$.	$C_6H_{12}O_3$.	$C_6H_{10}O_4$.	$C_6H_{10}O_5$.	$C_6H_{10}O_6$.	$C_6H_8O_7$.
Heptylic,	Œnanthylic,	. . .	Oxy-œnanthylic.	Pimelic,	. . .	Quinic,	Hydromeconic
$C_7H_{16}O$.	$C_7H_{14}O_2$.	$C_7H_{12}O_2$.	$C_7H_{14}O_3$.	$C_7H_{12}O_4$.	$C_7H_{12}O_5$.	$C_7H_{12}O_6$.	$C_7H_{10}O_7$.
. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
. . .	Myristic,	. . .	. . .	. . .	. . .	. . .	. . .
. . .	$C_{14}H_{28}O_2$.	. . .	. . .	. . .	. . .	. . .	. . .
. . .	Pentadecylic,	Cimicic,	. . .	. . .	. . .	. . .	. . .
. . .	$C_{15}H_{30}O_2$.	$C_{15}H_{28}O_2$.		. . .	. . .	. . .	. . .
Cetylic,	Palmitic,	Hypogaeic,	Linoleic,	. . .	. . .	. . .	. . .
$C_{16}H_{34}O$.	$C_{16}H_{32}O_2$.	$C_{16}H_{30}O_2$.	$C_{16}H_{28}O_2$.	. . .	. . .	. . .	. . .
. . .	Margaric,	. . .	. . .	Rocellic,	. . .	. . .	. . .
. . .	$C_{17}H_{34}O_2$.	. . .	. . .	$C_{17}H_{32}O_4$.	. . .	. . .	. . .
. . .	Stearic,	Oleic,	Ricinoleic,	. . .	. . .	. . .	. . .
. . .	$C_{18}H_{36}O_2$.	$C_{18}H_{34}O_2$.	$C_{18}H_{34}O_3$.	. . .	. . .	. . .	. . .

CHAPTER XXIII.

ORGANIC ACIDS.

675. The organic acids agree only in one particular, viz: the property of forming salts when they act upon the oxides or carbonates of the metals. The reaction consists in the exchange of one or more atoms of hydrogen for an equivalent amount of the metal; as,

$$HC_2H_3O_2 + KHO = KC_2H_3O_2 + H_2O.$$

I. A few organic acids contain hydrogen directly united to an acid radical, such as prussic acid, HCN.

II. Most organic acids contain hydroxyl (OH) or its equivalent, hydro-sulphuryl (SH), as in cyanic acid, CNOH, or in thio-cyanic acid, CNSH.

III. Ordinarily, the hydroxyl is linked to carbonyl CO, and forms the complex monovalent radical *carboxyl*, COOH, and this is in turn united with an alkyl radical, as in acetic acid,

$$CH_3 \cdot CO \cdot OH \text{ or } CH_3, COOH.$$

IV. The organic acids may be reckoned as derived from the primary alcohols by the oxidation of the groups CH_2OH; thus,

$$R', CH_2OH + O_2 = H_2O + R', COOH.$$

Monohydric alcohols give rise to acids which are also monohydric and monobasic; as, CH_3, COOH, acetic acid. Polyhydric alcohols give rise to polyhydric acids, which may be mono- or bi-basic, etc.; thus, glycol $(CH_2OH)_2$ may give rise to two dihydric acids (1) glycollic acid, $CH_2OH \cdot COOH$, which contains one alcoholic group, CH_2OH, unoxidized; (2) oxalic acid $(COOH)_2$ in which the oxidation is completed. The basicity of such acids is reckoned by the number of carboxyl groups they contain, because the replacable hydrogen of such acids is always associated with the radical carbonyl; thus glycollic acid is mono-basic, and oxalic acid is bi-basic.

V. However, there are many acids homologous with these that have no corresponding alcohol, but that are derived from ethers, as stearic acid; and there are still others obtained from plants and animals which can not be referred to the alcohols, as the meconic acid of opium.

VI. Among the organic acids are some which contain the radicals of the mineral acids, such as sulphurous acid $H(SO_2OH)$ and hyposulphurous acid $H(SOOH)$, associated with an alkyl radical. Thus, the CH_3 group which is found in acetic acid is also found in methyl sulphinric acid, CH_3SOOH, and in methyl sulphonic acid, CH_3SO_2OH. The endings, *inic* and *onic*, distinguish the lower and higher state of combination.

676. The salts which these acids form with the metals are (1) *normal* when all their basic hydrogen is exchanged for a metal, as potassium oxalate, $(COOK)_2$; (2) *acid* when their basic hydrogen is only partially exchanged, as acid potassium oxalate, $(COOH \cdot COOK)$; (3) *basic* when the acid radical does not completely saturate the metallic oxide; as,

$$2(C_2H_3O),\ 3PbO, \text{ basic plumbic acetate.}$$

677. The ethereal salts, which are usually known as the *compound ethers*, are formed by the substitution of an alkyl radical in place of the hydrogen in any one of hydroxyl groups of an acid; as, $C_2H_5 \cdot O \cdot CH_3CO$, ethyl acetate or acetic ether.

Inasmuch as glycerol, $C_3H_5(OH)_3$, contains a trivalent radical, the glycerine ethers may contain three monovalent acid radicals, which may be alike or different. These take the termination "in ;" as,

Glycerol, . .	$C_3H_5(OH)_3$.
Mono-acetin, .	$C_3H_5(OH)_2C_2H_3O_2$.
Di-acetin, . .	$C_3H_5(OH)(C_2H_3O_2)_2$.
Tri-acetin, . .	$C_3H_5(C_2H_3O_2)_3$

678. Negative radicals, such as Cl, CN, also replace the hydrogen of organic acids, and in three different ways:

I. To form *haloid compounds* as in the combination of acetic and hypoclorous anhydrides, producing chlor-acetate $= (CH_3CO)_2O + Cl_2O = 2(C_2H_3O, OCl)$.

II. To form *acid Halides*, etc., by exchange of hydroxyl for a negative radical, as when the chlorides of phosphorus convert acetic acid to acetyl chloride,

$$PCl_3 + 3(CH_3COOH) = P(OH)_3 + 3(CH_3COCl).$$

The acid radical, such as acetyl (CH_3CO), in chemical operations, may form acid anhydrides, like acetic anhydride $(CH_3CO)_2O$, or peroxides, like $(CH_3CO) \cdot O \cdot O \cdot (CH_3CO)$, or acid anhydrides containing two different acid radicals. All these have their analogues in inorganic compounds; as, KCl, chloride; $K \cdot O \cdot Cl$, hypochlorite; $K \cdot O \cdot K$, anhydride; $K \cdot O \cdot O \cdot K$, peroxide.

III. By exchange of an hydrogen atom in the alkyl radical, as when acetic acid, by the action of chlorine in the sunlight, forms in succession mono-chlor-acetic acid, $CH_2ClCOOH$; di-chlor-acetic acid, $CHCl_2COOH$; tri-chlor-acetic acid, Cl_3COOH. These substances are acids, resembling the acid from which they are derived.

The examples which have been used are taken from acetic acid, but we may believe that all saturated organic acids are susceptible of similar transformations. Besides these, there exist not only numerous isomeric modifications, but whole series of secondary and of unsaturated acids derived from the primary.

679. The fatty acids, $C_nH_{2n}O_2$ or $C_mH_{2m+1}COOH$, take this name because many of the higher members are found in the natural fats, as ethers of glycerol. They may be prepared (1) from fats by saponification, or (2) by decomposing the alcoholic cyanides, or (3), more frequently, by the oxidation of the monohydric alcohols.

The lower members of the series are volatile liquids of pungent odor. The members above C_{13} are not volatile, but may be distilled by means of a large volume of steam which carries their molecules over with it mechanically.

These acids after the fifth are insoluble in water, and thereby take on an oily character. Those above C_{10} are, at ordinary temperatures, solid bodies more or less resembling the fats. It may be noted that, with the succeeding terms, we find a decrease in specific gravity, but an increase in boiling and in melting points, which are noted in the table below:

FATTY ACIDS.

$C_nH_{2n}O_2$, ACIDS.	MELTING POINT °C.	BOILING P'NT °C.	SP. GR.	SOURCE.
$C\ H_2\ O_2$, Formic. .	8.5°	99°	1.233	Red ants.
$C_2\ H_4\ O_2$, Acetic. .	17°	118°	1.063	Alcohol.
$C_3\ H_6\ O_2$, Propionic. .	—21°	140.5°	.991	Ethyl cyanide.
$C_4\ H_8\ O_2$, Butyric. .	O	163°	.958	Sugar and cheese.
$C_5\ H_{10}O_2$, Valeric,(iso)	—16	185°	.947	Amyl alcohol.
$C_6\ H_{12}O_2$, Caproic. .	—2°	205°	.945	Cocoa-nut oil.
$C_7\ H_{14}O_2$, Œnanthylic.	—10°	224°	.934	Castor-oil.
$C_8\ H_{16}O_2$, Caprylic. .	16.5°	236°	.914	Cocoa-nut oil.
$C_9\ H_{18}O_2$, Pelargonic.	12.5°	253°	.906	Oil of rue.
$C_{10}H_{20}O_2$, Capric. .	30°	270°	.930	Fusel-oil.
. . . . .	. .	at 100mm		. . . . .
$C_{11}H_{22}O_2$, Undecylic .	28.5°	212.5°	. .	. . . . .
$C_{12}H_{24}O_2$, Lauric. .	43°	225°	.883	Bayberries.
$C_{13}H_{26}O_2$, Tridecylic .	45°	236°	. .	. . . . .
$C_{14}H_{28}O_2$, Myristic. .	54°	248°	. .	Nutmeg butter.
$C_{15}H_{30}O_2$, Pentadecylic	51°	257°	. .	. . . . .
$C_{16}H_{32}O_2$, Palmitic. .	62°	268.5°	. .	Palm-oil.
$C_{17}H_{34}O_2$, Margaric. .	66°	. .	. .	Cetyl cyanide.
$C_{18}H_{36}O_2$, Stearic. .	69.2°	287°	.74	Tallow.
$C_{19}H_{38}O_2$, Medullic. .	72.5°	. .	. .	Ox-marrow.
$C_{20}H_{40}O_2$, Arachidic .	75°	. .	. .	Pea-nuts.
C_{21}.	. .	. .	. .	. . . . .
$C_{22}H_{44}O_2$, Behenic. .	76°	. .	. .	Oil of Ben.
$C_{25}H_{50}O_2$, Hyænic. .	77°	. .	. .	Hyæna fat.
$C_{27}H_{54}O_2$, Cerotic. .	79°	. .	. .	Bees-wax.
$C_{30}H_{60}O_2$, Melissic. .	91°	. .	. .	Bees-wax.
$C_nH_{2n}O_2$. . . .	. .	. .	. .	. . . . .

680. Formic acid, $H \cdot COOH$, is found free in stinging nettles. It received its name because it was first obtained by distilling ants (*formica rufa*). It is a frequent product of the oxidation of organic substances, especially the carbohydrates, but is easiest obtained from oxalic acid ($COOH \cdot COOH = CO_2 + H \cdot COOH$). Very concentrated glycerol is heated to 110°, and a small quantity of crystallized oxalic acid added. (1) Mono-formin is produced, and carbonic anhydride evolved.

$$C_3H_5(OH)_3 + (COOH)_2, 2H_2O = 3H_2O + CO_2 + C_3H_5(OH)_2 \cdot (OCHO).$$

(2) This mono-formin, acted upon by fresh portions of oxalic acid, reproduces the glycerol, and evolves formic acid, which distills over

$$C_3H_5(OH)_2 \cdot (OCHO) + H_2O = C_3H_5(OH)_3 + H \cdot COOH.$$

Anhydrous formic acid is a colorless volatile liquid, of pungent odor, boiling at 100°C, and solidifying at 0°C; sp. gr. 1.23. The strongest hydrated acid is CH_2O_2, H_2O, which boils at 106°.

Formic acid may be regarded as the half aldehyde of carbonic acid, $H \cdot CO \cdot OH$. It reduces silver nitrate, and is itself oxidized to carbonic acid, $HO \cdot CO \cdot OH$.

681. Acetic acid, $C_2H_4O_2$ or $CH_3 \cdot COOH$, known and used from the earliest times in some form of *vinegar*, is a frequent product of the oxidation of many organic substances. In the old world it is manufactured on the large scale from the crude product obtained in the destructive distillation of wood (p. 166). On neutralizing this distillate with sodium carbonate, and evaporating, sodium acetate crystallizes out. This is decomposed by strong H_2SO_4, and again submitted to distillation. The distillate is *glacial* acetic acid so called, because it solidifies at 17°C to a transparent mass,

$$NaC_2H_3O_2 + H_2SO_4 = NaHSO_4 + C_2H_4O_2.$$

In this country it is prepared from dilute alcohol (8%), which is suffered to trickle slowly over hard wood shavings, contained in a large cask, through which the air is made to circulate freely. (Fig. 104.) At the start, a little yeast or old vinegar is added to sow its ferment, the *mycoderma aceti.* A temperature of about 30°C is maintained, and the process is completed in a few days.

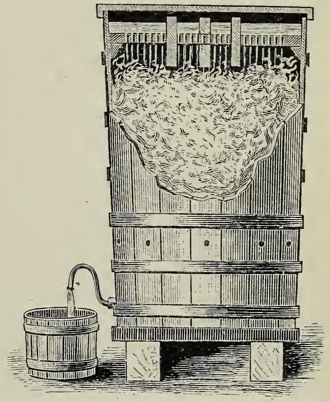


FIG. 104.

The best vinegar is that obtained from the natural souring of cider and wine. It contains from 3 to 15 per cent of the glacial acid. It has a well known odor and a pleasant acid taste.

The glacial acetic acid is a colorless liquid, capable of blistering the skin; sp. gr., 1.063; boiling point, 118°. Its vapor density at 300° is 30, being exactly that required by theory. Monohydrated acetic acid, $C_2H_4O_2$, H_2O, has a density of 1.079, but with either a greater or less amount of water the density diminishes, hence the specific gravity can not be used to determine the strength of acetic acid. Its strength is ascertained by observing the quantity of sodium carbonate which is required to neutralize a given amount of the acid.

Acetic acid forms a large number of important acetates, either by direct union with metallic oxides or by decomposition of their carbonates.

Potassium acetate, $KC_2H_3O_2$ or $CH_3 \cdot COOK$, is a white deliquescent body, soluble in alcohol. [Exp. 42, p. 36.]

Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, crystallizes in large

prisms, which are efflorescent, soluble in three times their weight of cold water.

Ammonium acetate decomposes, on heating, to water and acetamide, $CH_3 \cdot COONH_4 = H_2O + CH_3CONH_2$.

The alkalies also form so-called "acid salts," in which they take up an additional molecule of the acid; thus potassium di-acetate, $C_2H_3O_2K, C_2H_4O_2$, is formed when the normal acetate is dissolved in strong acetic acid and the mixture evaporated.

The acetates of iron, $Fe_2(OC_2H_3O)_6$, and of alumina, $Al_2(OC_2H_3O)_6$, are easily decomposed upon boiling their solutions into basic salts and free acetic acid. They find extensive employment as mordants in calico printing.

Lead acetate, $Pb(OC_2H_3O)_2, 3H_2O$, *sugar of lead*, is formed by dissolving litharge in vinegar. It has a sweetish but disagreeable metallic taste, and is poisonous. There are several basic salts obtained by digesting a solution of sugar of lead with lead oxide. These are also formed in the manufacture of white lead, being decomposed by carbonic anhydride into free acetic acid and the basic lead carbonate. See § 422.

Cupric acetate, $Cu(OC_2H_3O)_2, H_2O$, is moderately soluble in water, and is easily decomposed on boiling to a basic acetate. *Verdigris* is a mixture of basic cupric salts obtained by exposing metallic copper to the joint action of the air and vinegar.

TESTS. 1. On heating any dry metallic acetate in a hard glass tube, the odor of *acetone* will be perceived. The vapors are inflammable.

2. On heating a mixture of a metallic acetate and sulphuric acid with alcohol, acetic ether will be given off, and may be recognized by its pleasant odor.

682. Propionic acid, $C_3H_6O_2 = C_2H_5 \cdot COOH$, is obtained by boiling ethyl cyanide with sulphuric acid,

$$C_2H_5CN + 2H_2O + H_2SO_4 = NH_4HSO_4 + C_2H_5 \cdot COOH.$$

It is separated from its solution in water as an oily layer on the addition of calcium chloride. In other respects it strongly resembles acetic acid.

683. Butyric acid, $C_4H_8O_2 = C_3H_7 \cdot COOH$, has two isomeric forms which closely resemble each other.

Normal butyric acid is found either free or combined in the juices of many plants and animals, and is a frequent product of fermentation. The best method of preparing it is by the fermentation of sugar in contact with putrefying cheese. Lactic acid is first formed,

$$C_6H_{12}O_6 = 2C_3H_6O_3,$$

and is removed by the addition of chalk, as calcium lactate. After a time, this calcium lactate undergoes a second fermentation to calcium butyrate, $2C_3H_6O_3 = C_4H_8O_2 + H_2 + 2CO_2$. The peculiar offensive odors of rancid butter, limburger cheese, sauer kraut, etc., are due partly to butyric and lactic acids, and partly to the volatile acids with which they are usually associated,—valeric, caproic, caprylic, capric.

Iso butyric acid, $(CH_3)_2, CH \cdot COOH$, is found in St. John's bread, but is prepared by oxidation of the isobutyl alcohol obtained from fusel-oil.

684. Four isomeric forms of valeric acid have been prepared:

Propyl acetic (normal), $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$.

Isopropyl acetic, $(CH_3)_2, CH \cdot CH_2 \cdot COOH$.

Methyl ethyl acetic, $CH_3, C_2H_5 \cdot CH \cdot COOH$, or $CH_3, (CH_3 \cdot CH_2) \cdot CH \cdot COOH$.

Tri-methyl acetic, $(CH_3)_3 \vdots C \cdot COOH$.

The second of these is the ordinary "valerianic" acid. It occurs free in the valerian root to which it gives its characteristic odor. It is now prepared by the oxidation of isoamyl alcohol. Some of the salts are used in medicine, as nervous sedatives.

The isomers possible in the higher members rapidly increase, but after C_{12} few isomers are known.

685. Palmitic acid, $C_{16}H_{32}O_2 = C_{11}H_{31} \cdot COOH$, and
Stearic acid, $C_{18}H_{36}O_2 = C_{17}H_{35} \cdot COOH$,

are the most important of the non-volatile acids of this series, being found as palmitin and stearin in most solid fats and fixed oils. In their crude state, they are the principal constituents of "stearin candles," obtained by the saponification of lard and tallow. When purified from their alcoholic solutions, they crystallize in shining plates that melt, palmitic at 62°C, stearic at 69°.

686. The acrylic series of acids,

$$C_nH_{2n-2}O_2, \text{ or } C_mH_{2m-1} \cdot COOH,$$

contains upwards of twenty known acids which may be regarded as derived from ethylene and its homologues. The series takes its name from its lowest member, acrylic acid, $C_2H_3 \cdot COOH$, which is produced by the oxidation of acroleïn (p. 331). These acids are converted to the corresponding fatty acid by nascent hydrogen, acrylic becoming propionic acid,

$$C_2H_3 \cdot COOH + H_2 = C_2H_5 \cdot COOH,$$

and into two fatty acids by fusion with caustic potash, acrylic acid yielding potassium formate and acetate,

$$C_2H_3 \cdot COOH + 2KOH = CH_3 \cdot COOK + H \cdot COOK + \hat{H}_2.$$

Many of these acids are oily bodies which are found as glycerides accompanying those of the fatty acids. Of these acids the most important is:

Oleic acid, $C_{18}H_{34}O_2 = C_{17}H_{33} \cdot COOH$. It is found as olein in nearly all soft fats, like lard, and is the chief constituent of such fixed oils as olive, almond, cottonseed, etc. Free nitrous acid converts it to a solid iso-

mer, elaidic acid. This reaction serves also as a test for the presence of oleic acid in oils.

Fuming nitric acid oxidizes it with violence, producing a great variety of products, including nearly all of the volatile fatty acids, and those of the oxalic series. Olive-oil and other oils which contain olein, oxidize slowly in the air, probably giving rise to the same volatile acids which contribute to the odor and taste of the rancid fats. Very recently it has been found profitable in the manufacture of candles to convert oleic into palmitic acid by treatment with KOH.

687. The natural fats and fixed oils are, almost without exception, mixtures of several glycerides of the monobasic acids. Palmitin, stearin, and oleïn are nearly always found; and the character of a fat is largely dependent on the proportion in which it contains these three: the solid fats, as mutton-suet, are principally tri-stearin $(C_3H_5) \vdots O_3 \vdots (C_{18}H_{35}O)_3$; the fluids, like olive-oil, mainly tri-olein, $(C_3H_5) \vdots O_3 \vdots (C_{18}H_{33}O)_3$; palm-oil is chiefly tri-palmitin $(C_3H_5) \vdots O_3 \vdots (C_{16}H_{31}O)_3$. Some fats, as cocoa-nut oil, castor-oil, and the various butters, contain nearly all the fatty acids of an even number of carbon atoms from C_4 to C_{22} inclusive.

These oils are called *fixed* to distinguish them from the fragrant volatile or *essential* oils, lemon, wintergreen, etc., which contain no glycerol. They may be recognized by giving off the pungent vapors of acroleïn when thrown upon a heated stove-plate, and by their leaving a permanent grease spot when smeared upon paper. They are generally insoluble in water and alcohol, but are readily soluble in ether and carbon bisulphide. All float upon water, and are fluids above 100°C. Subjected to cold they undergo a partial separation; thus, the solid fat which separates out from olive-oil in the cold of winter is nearly pure palmitin.

In their pure state most of these bodies are colorless, odorless, and tasteless; but, as usually prepared, they contain foreign matters which impart a characteristic flavor and odor; thus, the odor of fish-oils is frequently due to the presence of valeric acid. When

fatty bodies are exposed to the air, the albuminous matters they contain putrefy, and induce a sort of fermentation by which the oils become rancid, liberating, or perhaps forming, the volatile acids, capric, valeric, butyric, etc.

Castor-oil contains ricinoleic acid, $C_{18}H_{34}O_3$, in place of oleic acid. It may be made to yield octylic alcohol and pelargonic acid, and is one of the few fixed oils which are soluble in alcohol. It is extensively employed, not only in medicine, but in the arts.

The drying oils are so called because they do not emit rancid odors on oxidation, but harden to a varnish-like mass. This property is increased by boiling them with $\frac{1}{20}$th their weight of litharge. They contain linoleic acid, $C_{16}H_{28}O_2$. The principal drying oils are linseed, hemp, and poppy. They are used in the manufacture of oil varnishes from copal and other resins, and, when mixed with white lead, zinc, etc., constitute the ordinary oil paints.

688. The separation of the acids, which are contained in the oils, is attended with special difficulties.

(1) The oils are first saponified and the glycerine removed. The usual process is by means of superheated steam, but sometimes a small proportion of lime or of sulphuric acid is first added.

(2) Most of the oleic acid is removed by pressure, the residue warmed and again compressed. The hard cake remaining is used in the manufacture of stearin candles.

(3) From such crude materials the volatile acids are separated by "partial saturation," followed by "fractional distillation." Half the crude mass is neutralized by an alkali, then added to the other portion and subjected to distillation. Naturally, the acid which has the lower boiling point will pass over first. If sufficient alkali has been added to saturate the higher carbon acid, nearly all of the distillate will consist of the volatile acids. By repeating this process, the lowest carbon acid will be obtained pure.

The separation of the higher fatty acids is effected by "fractional precipitation;" *e. g.*, suppose a mixture of palmitic and stearic acids. (1) It is dissolved in alcohol and about $\frac{1}{7}$ precipitated by magnesium acetate. This first seventh consists principally of the higher carbon acid (stearic). (2) The magnesian salt is decomposed by hydrochloric acid, the fatty acids washed and again dissolved in alcohol. (3) $\frac{1}{7}$ part (now $\frac{1}{49}$) is again precipitated, and the process repeated until two successive products exhibit identical

boiling points, specific gravities, etc. Heintz repeated these operations 33 times before obtaining pure stearic acid.

689. Soaps are the metallic salts of the higher carbon acids, palmitic, oleic, etc. The alkaline soaps only are soluble in water; the hard soaps contain soda, the soft soaps potash. These soaps, when added to much water, suffer a partial dissociation into a basic salt and a free alkali. The free alkali works cleansing upon the greasy articles submitted to its action, the basic salt forms the lather and assists in removing dirt by its mechanical action.

Usually, in preparing soft soaps, the crude fats are boiled with potash lye, glycerol is set free and passes into solution, together with the soap which is formed;

e. g., $C_3H_5 \vdots O_3 \vdots 3C_{18}H_{35}O + 3KOH =$
$$C_3H_5(OH)_3 + 3KC_{18}H_{35}O_2.$$

These products are boiled down to a thick mass, and usually contain an excess of alkali. The "glycerine soda soaps" are made by heating a similar mixture of fat and soda lye, to expel most of the water, and run into moulds; the glycerol remains mixed with the soap.

Ordinarily, the hard soaps are made by adding to either of these two crude soaps, while still in solution, a quantity of common salt. A soda soap at once separates out and rises to the top of the boiler's vat. It is drawn off into movable frames, in which it hardens sufficiently to be cut into bars. A portion of the acids used for the cheap bar soap is obtained from common resin. Castile soap is made from olive oil. The mottling which some varieties exhibit is due to the presence of iron oxide.

It is said that mottled soaps do not contain more than 30% of water. Some soaps contain as much as 70% of water. Cocoa-nut oil and soluble glass are added to soaps for the purpose of absorbing H_2O, and thereby increasing the weight.

Transparent soaps are produced by dissolving a dried soda soap in alcohol, distilling off the alcohol, and running the melted mass into moulds.

The soluble salts of lime, magnesia, and other dyad metals, when added to solutions of the alkaline soaps, immediately decompose them, and produce soaps which are insoluble in water and worthless for purposes of washing; as,

$$CaCl_2 + 2NaC_{18}H_{35}O_2 = Ca(C_{18}H_{35}O_2)_2 + 2NaCl.$$

Second Group—Dihydric Acids.

690. The primary glycols yield on oxidation acids which contain two hydroxyl groups (p. 332). These acids fall into two series: (1) The monobasic or lactic series, which contain but one COOH radical. (2) The bibasic or oxalic series, which contain two COOH groups.

691. The monobasic may be derived also from the fatty acids by substitution of OH for H in the alkyl radical. This is effected by first forming the mono-chlor derivative of the fatty acid, and then acting upon this product with moist silver oxide. When treated in this manner, propionic acid is converted to lactic acid.

$$(1)\ CH_3 \cdot CH_2 \cdot COOH + Cl_2 = HCl + CH_3 \cdot CHCl \cdot COOH.$$
$$(2)\ CH_3 \cdot CHCl \cdot COOH + AgHO = AgCl + CH_3 \cdot CHOH \cdot COOH.$$

The usual names of these bodies are formed by prefixing "oxy" to those of the fatty acids. Three have received special names,—glycollic or oxy-acetic, lactic or oxy-propionic, leucic or oxy-caproic acid. Half a dozen have been described. They resemble the fatty acids in their general reactions, and like them form only one series of metallic salts; but unlike them form three ethers with

the same alcohol radical, one acid and two neutral. The ethyl lactic ethers are:

CH_3	CH_3	CH_3	CH_3
|	|	|	|
$CHOH$	$CHOC_2H_5$	$CHOH$	$CHOC_2H_5$.
|	|	|	|
$COOH$	$COOH$	$COOC_2H_5$	$COOC_2H_5$.
Lactic acid.	Ethyl-lactic acid.	Mon-ethylic lactate.	Di-ethylic lactate.

Carbonic acid, $CO(OH)_2$, is theoretically the first member of this series; but, as either of its hydroxyl groups may enter into the carboxyl radical, $OH \cdot CO \cdot OH$, the acid is di-basic, and forms two series of metallic salts.

Several acids of this series are interesting because of their close relations to bodies found among the products of animal life.

692. Glycollic acid, $CH_2OH \cdot COOH$, is frequently found among the products of the decomposition of organic substances. It derives its name from glycocoll or glycocine, from which it was first obtained, but glycocine may be obtained from gelatine, and is itself amido-acetic acid, $CH_2NH_2 \cdot COOH$. Glycollic acid may also be prepared from glycol by partial oxidation, but more advantageously by carefully oxidizing ethyl alcohol with nitric acid.

Leucic acid, $C_4H_9 \cdot CHOH \cdot COOH$, is similarly related to leucine, which is amido-caproic acid, a substance found in various organs of animals (brain, liver, pancreas).

693. Two lactic acids only are required by theory, but four acids are known of the formula, $C_3H_6O_3$.

(1) The **ordinary lactic acid**, which is produced in large quantities by the fermentation of milk-sugar in presence of putrefying cheese, is ethylidene lactic acid, $CH_3 \cdot CHOH \cdot COOH$. It is found free in the gastric juice. It forms a syrupy, sour liquid; sp. gr., 1.25; miscible with water and alcohol. On being heated, two

molecules gradually lose water, becoming at last lactic anhydride, $C_3H_4O_2$, which is known as *lactide.* This lactic acid is optically inactive.

But (2), there exists in the juice of flesh (Liebig's extract) **para lactic acid,** which turns the plane of polarized light to the left. These two acids are otherwise strikingly alike, and are physical isomers. They yield identical products upon being decomposed by chromic mixture, producing formic and acetic acids.

(3) **Ethylene lactic acid,** $CH_2OH \cdot CH_2 \cdot COOH$ is also found in small quantities in flesh extract, and has been prepared synthetically from its cyanide. When the flesh extract is oxidized, malonic acid is formed,

$$CH_2OH \cdot CH_2 \cdot COOH + O_2 = H_2O + COOH \cdot CH_2 \cdot COOH.$$

(4) **Hydracrylic acid** may be obtained in crystalline plates from glyceric and from acrylic acids by successive treatment with HI and AgHO. On oxidation it yields oxalic and carbonic acids.

The zinc salts of these isomeric acids show considerable differences in solubility. This property is used to separate them from their mixed solutions.

694. The oxalic series of bibasic acids, $C_nH_{2n}(COOH)_2$, contains about a dozen members. The lower carbon acids may be obtained by the complete oxidation of the corresponding glycols; the higher members are generally prepared by oxidizing fatty and resinous bodies with nitric acid. They are for the most part non-volatile solids, crystallizable, and soluble in water. They form both acid and neutral salts and ethers; as,

COOH	COOH	COOH	COOK	$COOC_2H_5$.
|	|	|	|	|
COOH	COOK	$COOC_2H_5$	COOK	$COOC_2H_5$.
Oxalic acid	Acid potassium oxalate.	Ethyl oxalic acid.	Normal potassium oxalate.	Ethyl oxalate.

695. Oxalic acid, $(COOH)_2$, is widely distributed in plants, especially in the sorrel and rhubarb, as calcium oxalate. It is also found in urinary calculi as a calcium salt. It is produced by the oxidation of a large number organic substances, and may be prepared by heating sugar, starch, cellulose, etc., with five times their weight of strong nitric acid,

$$2C_6H_{10}O_5 + 9(H_2O \cdot N_2O_5) = 6C_2O_4H_2 + 9N_2O_3 + 13H_2O.$$

On the large scale it is manufactured by heating a mixture of saw-dust and caustic soda. The sodium oxalate which forms is decomposed by boiling with slaked lime, and the resulting calcium oxalate by means of sulphuric acid.

Oxalic acid dissolves in less than its own weight of boiling water. On cooling, the greater part crystallizes out in prisms, $C_2O_4H_2$, $2H_2O$. If this acid be carefully heated, (1) it loses its water of crystallization at 100°C; (2) the remaining anhydrous acid sublimes undecomposed at 150°C, but (3), if rapidly heated to higher temperatures, is completely broken up,

$$2C_2O_4H_2 = H_2O + 2CO_2 + CO + H \cdot COOH.$$

Similar decompositions are effected by most dehydrating agents, yielding among other products carbonous oxide and formic acid. Oxalic acid is, therefore, a strong reducing agent; its solutions reduce salts of the noble metals.

Exp. 198.—Repeat Exp. 196, page 268, using oxalic acid in place of ferrous sulphate. Add H_2SO_4. Notice the different rapidity with which the permanganate is bleached when poured into a warm or a cold solution of oxalic acid.

Oxalic acid forms with most of the dyad metals only normal salts; as, C_2O_4Ca, $4H_2O$. With monovalent metals, as potassium, normal salts; as, $C_2O_4K_2$, $2H_2O$, acid salts; as, C_2O_4HK, $2H_2O$, and also hyper-acid, C_2O_4HK, $C_2O_4H_2$, $2H_2O$. The solutions of

the normal alkaline oxalates are neutral to litmus, and hence oxalic acid is employed in volumetric analyses of alkalies.

All the oxalates are decomposed by heat without separation of carbon, (1) evolving CO and leaving metallic carbonates, as those of the alkalies; (2) those carbonates which are also decomposed by heat (Zn, Mg, Ca), leaving, when strongly heated, only metallic oxides; as, ZnO; (3) evolving CO_2, and leaving only the metals. The last reaction affords a method for obtaining pure metallic cobalt and other metals.

The alkaline oxalates are soluble in water, the other oxalates (except Fe) are nearly insoluble in water, but are readily soluble in solutions which contain free mineral acids. Calcium oxalate is, however, not soluble in excess of oxalic or acetic acids, and hence $CaCl_2$ is a delicate test for the presence of oxalic acid in solutions containing no acids except these.

Oxalic acid and its soluble salts are used in calico printing, in the manufacture of blue ink, and in bleaching straw goods, also for cleansing brass, and for taking iron mould out of cloth. The acid potassium oxalate, which is used for the last purpose, is sold under the names of "salt of sorrel" and "salt of lemons." It is sometimes used in making the cheap "lemonade" at fairs, etc.

Oxalic acid and its soluble salts are highly poisonous. The proper antidote is precipitated chalk or whiting.

696. Malonic acid, $COOH \cdot CH_2 \cdot COOH$, may be obtained from monochloracetic acid by (1) boiling this with potassium cyanide, and (2) by heating the cyanacetic acid thus produced with an alkali. It and its ketonic derivative, mesoxalic acid, $COOH \cdot CO \cdot COOH$, are chiefly interesting because of their relations to lactic and malic acids, and to the compound ureas.

697. Succinic acid has two modifications. The ordinary succinic acid, $COOH \cdot (CH_2)_2 \cdot COOH$, occurs ready formed in amber and in many plants. It is obtained by the dry distillation of amber (yield 4%), and is one of the products of the long-continued action of nitric acid upon the fats. It is advantageously prepared by the fermentation of calcium malate or tartrate with old cheese. The calcium succinate which results is decom-

posed by sulphuric acid. The succinic acid remains in solution, and is purified by recrystallization and by sublimation. It forms colorless prisms which melt at 180°C and boil at 235°, undergoing decomposition into water, and succinic anhydride $(CH_2 \cdot CO)_2O$, which distill over. The anhydride, on long boiling with water, is reconverted into the acid. Ammonium succinate, when boiled with neutral aluminium and ferric solutions, completely precipitates these metals as basic succinates.

698. Three other series of bibasic acids are known, each of which contains from three to ten members:

Fumaric series, $C_nH_{2n-2}(COOH)_2$.
Malic series, $C_nH_{2n-1}OH, (COOH)_2$.
Tartaric series, $C_nH_{2n-2}(OH)_2, (COOH)_2$.

Besides these there are a few tribasic acids, as citric acid, $C_nH_{2n-2}(OH)(COOH)_3$, as well as a number of higher basicity, which have not as yet been arranged in series.

699. Fumaric and maleic acids, $C_4H_4O_4$, are isomers produced by the dry distillation of malic acid,

$$C_4H_6O_5 = H_2O + C_4H_4O_4,$$

and are converted by nascent hydrogen, H_2, into succinic acid, $C_4H_6O_4$. Fumaric acid also occurs in the free state in various plants, as in Iceland moss.

700. Oxalic, malic, tartaric, and citric acids are generally associated together by twos and threes in the sour juices which exist in the stalks, leaves, and fruits of plants, sometimes in the free state, but more frequently in combination with calcium or potassium. They are the chief sources of the potassium carbonate which is found in the ashes of plants.

701. Malic acid, $C_4H_6O_5 = COOH \cdot CHOH \cdot CH_2 \cdot COOH$, is found in many sour fruits (unripe apples, gooseberries,

etc.,) but is especially abundant in the nearly ripened berries of the mountain ash and of the sumach. It may also be prepared advantageously from the expressed juice of any one of these, also artificially by the reduction of tartaric acid, and by the oxidation of succinic acid. The latter process yields an acid optically inactive; the ordinary malic acid rotates polarized light to the left. The malic acids are white deliquescent bodies, soluble in alcohol, and of an agreeable acid taste. They are easily reduced to succinic, butyric, and acetic acids.

702. Asparagin is a crystallizable substance present in asparagus, and in the young shoots of many plants. On boiling it with acids or with alkalies, it becomes aspartic acid, but if either asparagin or aspartic acid is treated with nitrous acid, malic acid is produced. These are, therefore, amide bodies. Any one of these three, when fermented with old cheese, yields succinic acid, and this in turn butyric acid, etc. These relations are supposed to play an important role in the growth of plants, and are partially exhibited by their structural formulæ:

Asparagin,	$COOH \cdot CHNH_2 \cdot CH_2 \cdot CONH_2$.
Aspartic acid,	$COOH \cdot CHNH_2 \cdot CH_2 \cdot COOH$.
Malic acid,	$COOH \cdot CHOH \cdot CH_2 \cdot COOH$.
Succinic acid,	$COOH \cdot CH_2 \cdot CH_2 \cdot COOH$.

703. Tartaric acid,

$$C_4H_6O_6 = COOH \cdot CHOH \cdot CHOH \cdot COOH$$

occurs especially in the grape. It is manufactured from the crude acid potassium tartrate or *argol*, which is deposited in red crusts during the ripening of wines. This salt, which requires 240 parts of cold water for its solution, dissolves in 14 parts of boiling water. It is purified by dissolving in boiling water containing animal charcoal, filtered and recrystallized. It is sold under the name of cream of tartar, and is largely used in baking

powders. The normal salt, $K_2C_4H_4O_6$, is soluble in less than half its weight of cold water.

The acid is prepared by boiling the purified cream of tartar with powdered chalk, first producing insoluble calcium tartrate and normal potassium tartrate.

$$2KHC_4H_4O_6 + CaCO_3 = H_2O + CO_2 + \underline{CaC_4H_4O_6} + K_2C_4H_4O_6.$$

Calcium chloride is now added to decompose the latter, and the calcium tartrates are digested with dilute sulphuric acid. $CaC_4H_4O_6+H_2SO_4=\underline{CaSO_4}+H_2C_4H_4O_6$. The tartaric acid is filtered off from the insoluble calcium sulphate, and on evaporation crystallizes in large monoclinic prisms, easily soluble in water. On heating to 135°C it is changed to its isomer, metatartaric acid, an uncrystallizable gum-like mass. At 150° it loses water, and changes to its anhydride, $C_4H_4O_5$, and at higher temperatures undergoes decomposition, yielding a great number of products, among which are pyrotartaric, acetic, and formic acids, and evolving a characteristic odor of burnt sugar. Tartaric acid is readily oxidized, yielding in most cases formic acid, and hence acts reducing on the noble metals.

Exp. 199.—Add to a neutral solution of silver nitrate a solution of neutral ammonium tartrate, and dissolve this in ammonia, avoiding excess. Now heat a portion of this solution, diluted, if necessary, in a perfectly clean test-tube to a temperature nearly, but not quite, its boiling point for some time. Metallic silver will separate out and form a brilliant mirror on the glass.

704. The normal tartrates of the alkalies and Rochelle Salt, $KNaC_4H_4O_6$, $4H_2O$, are easily soluble; the acid tartrates (except Na), but sparingly (p. 207). Heated, they first blacken, but in free air the fixed alkaline tartrates at last burn to pure white carbonates.

Tartar emetic, $KSbOC_4H_4O_6$, is made by boiling cream of tartar with antimonous oxide, § 269. It is poisonous. Tartaric acid and its soluble salts are used in calico printing, in tinning pins, in baking powders, and in medicine.

705. There are four physical isomers of tartaric acid, which are identical in chemical properties with the ordinary acid.

1. Dextro-tartaric acid, so called because its aqueous solution turns the plane of polarized light to the right.
2. Lævo-tartaric acid turns the plane of polarization to the left.
3. Racemic acid, which is optically inactive, but which may be resolved into the two former.
4. Inactive tartaric acid, which has no effect on polarized light, but which can not be so separated.

When Dextro tartaric acid is heated with a little water to 175° under pressure, it is converted into a mixture of two inactive acids. On evaporation, racemic acid crystallizes out first, the inactive acid remaining in solution may be entirely converted to racemic acid by long boiling.

If equal quantities of racemic acid are saturated with soda and ammonia separately, crystals are obtained which are identical in form, but if the two solutions are mixed a double salt,

$$NaNH_4C_4H_4O_6,\ 4H_2O,$$

is formed, which, on evaporation, yields two crops of rhombic crystals exactly alike, except that the hemihedral faces, h,h, of one are turned to the right, and those of the other to the left, so that one is a sort of reflected image of the other. If the two kinds of crystals are separated and dissolved in water, they will each deflect a polarized ray of light to the same extent, but in opposite directions; that is, one now contains dextro-tartaric

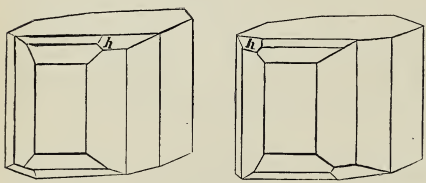


FIG. 105.

acid, and the other lævo-tartaric acid, each of which may be obtained in the free state by first precipitating them by $CaCl_2$, and subsequently decomposing the salt with H_2SO_4. Moreover, if equal amounts of dextro and lævo-tartaric acids be mixed together in solution, racemic acid will be produced, with elevation in temperature, showing a combination has taken place.

706. Citric acid, $C_6H_8O_7 = (C_3H_4OH)(COOH)_3$, occurs free in lemons ($5\frac{1}{2}\%$), currants, and other acid fruits. It is prepared from lemons (1) by boiling the juice to remove albuminous matters; (2) saturating the clarified liquid while hot with calcium carbonate; and, (3) finally, decomposing the calcium citrate with sulphuric acid. The filtered solution yields, on evaporation, colorless prisms, which melt at 100°C, and become anhydrous; heated above 175°C, aconitic acid, $C_6H_6O_6$, identical with that obtained directly from monkshood; and at higher temperatures, other products. Citric acid forms three series of salts, those of potassium having the composition: (Normal) $K_3C_6H_5O_7, H_2O$,
(Di-potassic) $K_2HC_6H_5O_7$,
(Monopotassic) $KH_2C_6H_5O_72H_2O$.

Tartaric and citric acids are used in dyeing and in calico printing, and their salts are used in medicinal preparations. Solutions of ammonium citrate are used in the analyses of fertilizers as solvents for the so-called "reverted phosphates."

Recapitulation.

(1) All acids contain H, replaceable by metals; as, in HCl, HCN, H, $C_2H_3O_2$.

(2) The best known of the organic acids contain the group hydroxyl (OH); as, $HO \cdot C_2H_3O$.

(3) This hydroxyl may be contained not only in the acid radical COOH, *carboxyl*, or SO_2OH, etc., but it may also be a part of the alcoholic radical CHOH, etc.

(4) The hydrogen of such groups as COOH, SO_2OH, are easily replaced by metallic oxides, but this is not the case with alcohol radicals like CHOH.

(5) Accordingly, the words mono-hydric, di-hydric, etc., refer to the number of hydroxyl (OH) molecules present in an acid.

(6) Accordingly, also, the words mono-basic and di-basic, etc., refer to the number of H atoms present in an acid which may be replaced by metallic hydroxides, like KOH.

(7) The best known organic acids contain the carboxyl COOH.

(8) The hydroxyl of this group may be replaced by Cl, by NH_2, etc.; as, $CH_3 \cdot COCl$.

(9) If hydroxyl is supposed to be removed, an acid radical remains; as, $C_2H_3O =$ acetyl.

(10) Such a group may be united to any other equivalent group by linking oxygen to form acid anhydrides, ethereal salts, etc.

(11) An acid which contains two hydroxyl molecules or more may suffer partial or total displacement of its hydroxyl by Cl, or by NH_2, etc., and thus give rise to many different compounds.

(12) The H in the alkyl radical may be replaced by Cl, NH_2, etc., without change in the acid radical COOH; as, $CH_2Cl \cdot COOH$.

(13) It is possible that the H in an organic acid may be replaced (1) by positive atoms, like the metals, to form salts, such as the acetates; (2) by negative radicals, like the haloids, to form new acids, like the chlor-acetic acids; or (3), by both of these substitutions; as the chlor-acetates.

(14) Very many acids of high carbon percentage may be converted into two or more of lower carbon content (by heating alone or with KHO); as oleic to palmitic.

(15) Most of these acids may be arranged in series whose members exhibit gradational properties; as, the fatty acid series, the lactic series, etc.

N. B. Not a hundredth part of the organic acids known have been mentioned in this book.

CHAPTER XXIV.

AMINES AND AMIDES.

707. Three radicals may be obtained from ammonia, NH_3, which were once termed amidogen $(NH_2)'$, imidogen $(NH)''$, and nitril $(N)'''$. Besides these, salts, like NH_4Cl, are supposed to contain the univalent radical ammonium $(NH_4)'$.

When these radicals combine with positive radicals, AMINES are formed; with negative radicals, AMIDES; and with both positive and negative, ALKALAMIDES (p. 300).

708. The Amines are strong bases, which may be regarded as ammonias, containing in place of one, two, or three atoms of hydrogen in NH_3, a like number of alkyl radicals. The compounds formed by the successive replacement of a hydrogen atom in the NH_3 group, are termed primary, secondary, and tertiary; as, CH_3NH_2, methyl amine (primary); $(CH_3)_2NH$, di-methyl amine (secondary); $(CH_3)_3N$, tri-methyl amine (tertiary).

The prefixes mono, di, tri, etc., denote the number of NH_3 groups, which enter into the new compound, and also indicate the number of nitrogen atoms present; as, ethene diamine, $(C_2H_4)''(NH_2)_2 = C_2H_4N_2H_4$.

There are also compounds which are related to both amines and and amides, as $CH_2NH_2 \cdot CONH_2 =$ amido acetamide. These ammonia derivatives are more widely distributed in plants and in animals than is usually supposed. Doubtless both amines and amides play an important part in the formation of the albuminoids, and other organic compounds containing nitrogen, as they are always found among the products of their decomposition. Most

of the so-called *active principles* of plants, like nicotine and morphine, are amines. The amides are fitted by their flexible character to be of great physiological importance; they are especially abundant in the young shoots of plants, and in the glands of animals. For examples, *asparagin*, the amide of malic acid, is frequently found in plants; and *leucine*, the amide of caproic acid, is one of the products of the decompositions of albuminoid substances, as is also urea, or carbamide.

709. The amines strikingly resemble ammonia in odor and in the alkaline properties of their solutions, but their vapors burn with a continuous flame (Exp. 49), and they are stronger bases than ammonia. Like ammonia, they combine directly with the acids, forming salts on the type of the ammonium (NH_4) compounds; thus, ethyl ammonium chloride, $C_2H_5NH_3Cl$, is similar in structure to ammonium chloride, HNH_3Cl.

These compounds are easily formed by heating in closed vessels an alkyl iodide with an alcoholic solution of ammonia. For example, ethyl iodide and ammonia yield chiefly ethyl ammonium iodide, $C_2H_5I + NH_3 = C_2H_5NH_3I$. In practice several amines are formed at the same time. For example:

$C_2H_5NH_3I$, ethyl-ammonium iodide (primary).
$(C_2H_5)_2NH_2I$, di-ethyl ammonium iodide (secondary).
$(C_2H_5)_3NHI$, tri-ethyl ammonium iodide (tertiary).
$(C_2H_5)_4NI$, tetrethyl ammonium iodide.

This is probably due to a progressive action, whereby the amine compound first produced reacts upon the other substances present.

710. The tetrethyl ammonium iodide may be converted by moist silver oxide into tetrethyl ammonium hydroxide, $(C_2H_5)_4NI + AgHO = (C_2H_5)_4NOH + AgI$. This hydroxide may be obtained as a stable deliquescent solid, which resembles caustic potash rather than ammonia, forming true soaps, and expelling ammonia from its compounds. Heated to 100°, it breaks up into triethylamine, ethylene and water,

$$(C_2H_5)_4NOH = (C_2H_5)_3N + C_2H_4 + H_2O.$$

It has not been found possible to obtain a body of the formula NH_5, nor of $(C_2H_5)_5N$. The fifth bond of "ammonium" nitrogen, seems to require a negative radical, like I or NO.

711. The primary amines may be obtained pure by the action of nascent hydrogen upon the nitrils; thus, aceto-nitril, $C_2H_3N + H_4 = C_2H_5NH_2$, ethylamine. On the other hand, they are converted by nitrous acid into the corresponding alcohol; as, $C_2H_5NH_2 + HNO_2 = \widehat{N}_2 + H_2O + C_2H_5OH =$ ethyl alcohol. This reaction is important, because it is one of the steps in synthesis by which any alcohol can be formed from the next lower in the series. It serves also to distinguish the primary amines, inasmuch as the secondary and tertiary amines so treated form only nitroso-compounds; as,

$$(CH_3)_2NH + HNO_2 = H_2O + N(CH_3)_2NO = \text{nitroso-dimethylamine.}$$

The simplest of all these compounds is *hydroxyl-amine*, NH_2OH, which is easily formed; as, the hydrochloride, $NH_3O \cdot HCl$, by reducing nitric ether with tin and hydrochloric acid. It is a strong base, not as yet isolated, which may be regarded as an ammonia in which an atom of H has been replaced by hydroxyl.

712. The methylamines are found in many plants, as *chenopodium vulvaria*, *ergot*, and usually among the products of decay, as in rotting grain.

Methylamine, CH_3NH_2, is an easily inflammable gas, liquid below 0°C. Water at 12.5°C absorbs 1150 times its volume of the gas, forming a solution which has most of the properties of aqua ammonia.

Di-methylamine, $(CH_3)_2NH$, is isomeric with ethylamine, $C_2H_5NH_2$, but has a lower boiling point.

Tri-methylamine, $(CH_3)_3N$, is found largely in herring pickle, to which it gives its peculiar odor, and is prepared on a large scale from the dry distillation of the

residue left in making beet sugar. It is a liquid, boiling at 9.3°C, exceedingly soluble in water. It is isomeric with propyl amine, $C_3H_7NH_2$.

713. **The primary ethyl amine,** $C_2H_5NH_2$, may be obtained by heating ethyl isocyanate with caustic potash, $C_2H_5CNO + 2KHO = K_2CO_3 + C_2H_5NH_2$. The other ethyl amines are derived from this by heating with ethyl bromide.

714. **Normal propylamine,** $CH_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$, is prepared from ethyl cyanide by the action of zinc and hydrochloric acid, $C_2H_5CN + H_2 = C_3H_7NH_2$. It is an alkaline liquid; sp. gr., 0.73; boiling point, 49°C. It has five isomers. The article usually sold by this name is tri-methyl amine.

There are also higher homologues,—butyl amine, amyl amine, etc. All these resemble those described, but are of greater density and higher boiling point.

715. **Precisely analogous** to the amines are the phosphines formed from PH_3 by the action of the alcoholic iodides; as, $P(C_2H_5)_3$, tri-ethyl phosphine.

Tri-ethyl phosphine is a valued test for carbon di-sulphide, with which it forms red crystals, $(C_2H_5)_3PSCS$.

716. **Arsenic** forms bases somewhat similar to the amines; as,

$(CH_3)_3As$, tri-methyl arsene, and
$(CH_3)_4AsOH$, tetra-methyl arsonium hydrate.

Cacodyl, $(CH_3)_2As \cdot As(CH_3)_2$, is obtained in small quantity by the dry distillation of arsenious oxide and potassium acetate. The principal product is cacodyl oxide,

$$4(CH_3COOK)+As_2O_3=2K_2CO_3+2CO_2+(2CH_3, As)_2O.$$

This impure oxide evolves poisonous vapors of a disagreeable odor, which are spontaneously inflammable.

With HCl it yields Cacodyl chloride, $(CH_3)_2AsCl$, from which pure cacodyl may be obtained by the action of zinc filings,

$$2(CH_3)_2AsCl + Zn = ZnCl_2 + (CH_3)_2As \cdot As(CH_3)_2.$$

An ethyl cacodyl is also known; both are colorless liquids, somewhat heavier than water, evolving vapors of disgusting odor, and spontaneously inflammable in the air.

Organo-Metallic Compounds.

717. Some of the metals, but not all, form basic compounds with alkyl radicals. This union is brought about (1) by heating in a stone vessel an alkyl iodide with a positive metal or its sodium alloy; as,

$$2C_2H_5I + ZnNa_2 = 2NaI + (C_2H_5)_2Zn, \text{ or}$$

(2), by decomposing a zinc compound so formed by the chloride of a less positive metal; as,

$$2(C_2H_5)_2Zn + 2PbCl_2 = 2ZnCl_2 + (C_2H_4)_4Pb.$$

These compounds are, for the most part, volatile bodies, spontaneously inflammable when exposed to the air, and exceedingly active as chemical re-agents.

The compounds of zinc are usually taken as a starting-point. Zinc methyl, $(CH_3)_2$, Zn.; zinc ethyl $(C_2H_5)_2$, Zn., etc., resemble each other, like the members of other series. The lower members are colorless liquids, somewhat heavier than water, and of low boiling point (from 46° to 200°), and yielding white vapors of a peculiar, unpleasant odor.

718. The readiness with which these bodies are decomposed by water, and by the haloid elements, especially fit them for the synthesis of organic compounds. For examples: (1) Zinc methyl $(CH_3)_2Zn$, treated with free iodine, yields ZnI_2, and methyl iodide, CH_3I = an alkyl haloid; (2) by the reaction of this upon a fresh

portion, a paraffin is formed, $2(CH_3I) + (CH_3)_2Zn = ZnI_2 + 2(C_2H_6)$, ethane. Similarly, we may form from the acid chlorides (3) ketones; as,

$$2CH_3COCl + (C_2H_5)_2Zn = ZnCl_2 + 2(CH_3 \cdot CO \cdot C_2H_5) = \text{methyl-ethyl ketone};$$

or (4), in the presence of water, tertiary alcohols; as,

$$CH_3COCl + 2(CH_3)_2Zn + 2H_2O = CH_3ZnCl + CH_4 + Zn(OH)_2 + CH_3 \cdot COH \cdot (CH_3)_2 = \text{tertiary butyl alcohol.}$$

These zinc organic compounds form, with sodium and potassium, mixtures which contain similar compounds of the alkalies. These mixtures, exposed to carbonic anhydride, yield a salt of the fatty acid next higher in the series; *e. g.*,

$$C_2H_5Na + CO_2 = C_2H_5COONa = \text{sodium propionate.}$$

719. The amides may be obtained (1) by heating ammonium salts to expel one molecule of water; as, ammonium acetate $= CH_3COONH_4 - H_2O = CH_3CONH_2$ becomes acetamide; and (2), by the action of ammonia upon acid chlorides; as, acetyl chloride,

$$CH_3COCl + NH_3 = HCl + CH_3CONH_2.$$

Hence, they contain both acid and ammonia radicals, and act as indifferent bodies, capable of uniting with acids or with metals.

720. The mono-hydric acids can each form one primary amide by the substitution of NH_2 for hydroxyl; as, form-amide, $HCONH_2$, from formic acid, $HCOOH$, and acetamide, whose preparation has already been indicated.

The amides of the monobasic acids are generally solids, crystallizable, volatile, frequently of characteristic odor. They are characterized by the fact that on being boiled with the alkalies, they reproduce the acids or the ammonia salts from which they were obtained; as,

$$CH_3CONH_2 + H_2O = CH_3COOH + NH_3.$$

721. Secondary monamides contain amidogen united to two monovalent radicals; as, di-acetamide, $(CH_3CO)_2NH$. *Alkalamides* are formed by heating the amines with acid ethers or chlorides, as;

$$CH_3COCl + C_2H_5NH_2 = HCl + (C_2H_5), (C_2H_3O)NH.$$

They contain both acid and alkyl radicals. The *imides* contain one bivalent acid radical; as,

lactimide, $(C_3H_4O):NH$; succinimide, $C_2H_4(CO_2)_2NH$.

722. The tertiary monamides contain triatomic nitrogen. They may contain three monovalent carbon radicals, or one monovalent and one divalent; as, triacetamide, $(CH_3CO)_3N$. They are formed by heating the secondary amides with acid chlorides; as,

$$(C_2H_5)(C_2H_3O)NH + CH_3COCl =$$
$$HCl + (C_2H_5)(C_2H_3O)_2N = \text{ethyl diacetamide.}$$

The nitrils contain a trivalent carbon radical, and may be formed from primary amides by the action of phosphoric anhydride.

723. The nitrils are identical with the cyanogen ethers, aceto-nitril, C_2H_3N, being the same as methyl cyanide, CH_3CN. They are also prepared by heating potassium cyanide with a potassium alkyl sulphate, like KCH_3SO_4; but when so prepared, they are accompanied by their metamers, the isocyanides. These latter are usually prepared from a mixture of chloroform and an alcoholic solution of potassium hydroxide with an amine, and hence are called the carb-amines.

The two series differ at all points. The carbamines are poisonous, of nauseous odor, of great chemical activity, decomposed by boiling with water plus an acid into formic acid, and an amine salt; as, $CH_3 \cdot NC + H_2O + HCl = HCOOH + CH_3NH_2 \cdot HCl$, methylamine hydrochloride, and by AgHO into a cyanate; as, CH_3CNO.

The nitrils are not oxidized by AgHO. They are decomposed by boiling with water plus an acid into an ammonium salt, and

the fatty acid, which is next higher in the carbon series; as, from methyl cyanide, $CH_3CN + H_2O + HCl = NH_4Cl + CH_3COOH =$ acetic acid. Their odors are not unpleasant, and they are not regarded as poisonous; they are also of higher boiling point than the corresponding isocyanides.

724. Acids containing one or more hydroxyl groups may give rise to a great variety of amide compounds, which are structurally derived from their ammonium compounds by the removal in succession of one or more molecules of water. For example: the acid ammonium succinate, $CONH_4$, C_2H_4, COOH, yields an acid amide; succinamic acid, $CONH_2$, C_2H_4, COOH, and then succinimide, $C_2H_4(CO)_2NH$. The normal ammonium succinate, $C_2H_4(COONH_4)_2$, yields first succinamide,

$$C_2H_4(CONH_2)_2,$$

and then succino-nitril, $C_2H_4(CN)_2$.

725. The amic acids are intermediate between the acids of the fatty and lactic series, and are termed *alanines.* For example, amid-acetic acid, formed by the action of dry ammonia upon chlor acetic acid,

$$CH_2Cl \cdot COOH + 2NH_3 = NH_4Cl + CH_2NH_2 \cdot COOH,$$

is glycocine, and may be converted to glycollic acid by oxidation with nitrous acid.

CH_3	CH_2NH_2	CH_2OH	$CH_2OH.$
|	|	|	|
COOH	COOH	COOH	$CONH_2.$
Acetic acid.	Glycocine.	Glycollic acid.	Glycollamide.

The same relations exist between propionic acid, alanine, and lactic acid; caproic acid, leucine and leucic acid.

726. Amid-acetic acid, or glycocine, is obtained by boiling hippuric acid with hydrochloric acid and water:

$$C_7H_5O \cdot NH \cdot CH_2 \cdot COOH + H_2O =$$
$$C_6H_5COOH \text{ (benzoic acid) } + CH_2NH_2 \cdot COOH.$$

It forms rhombic prisms, which have a sweetish taste, and combines both with acids and bases. It forms many products by substitution, among which are to be noted (1) its amide, $CH_2NH_2 \cdot CONH_2$, amido-acetamide, which is formed by heating glycocine with alcoholic ammonia to 155°C; (2) its alkyl derivatives; as, *sarcosine* =

$$CH_2 \cdot NHCH_3 \cdot COOH,$$

which is obtained by heating creatine with barium hydroxide. *Creatine* is formed artificially by heating sarcosine with cyanamide, and is, therefore, methyl-glycocine-cyanamide,

$$NH_2, NH : CN(CH_3) \cdot CH_2 \cdot COOH = C_4H_9N_3O_2.$$

It is always present in meat juice, and may be prepared from the flesh extracts. *Creatinine*, $C_4H_7N_3O$, is a decomposition product of creatine, and, as such, is found not in flesh, but in urine (0, $\frac{1}{4}$%).

These bodies probably contain the same complex radical, guanidine $(NH : C : (NH)_2)''$, as in guanine, $C_5H_5N_5O$, which is found along with uric acid in guano. Allied to these, but containing the radical of urea $(NH_2 \cdot CO \cdot NH_2)$, are the three following, which also occur in flesh juice; viz,

Carnine, $C_7H_8N_4O_3$, oxidized by nitric acid to *sarcine*, or hypoxanthine, $C_5H_4N_4O$, and *xanthine*, $C_5H_4N_4O_2$.

727. Homologous with xanthine are two widely distributed vegetable bases; viz, *Theobromine*, $C_7H_8N_4O_2$, which is the active principle of the cacao beans, and its methyl derivative, *caffeine*, $C_8H_{10}N_4O_2$, the alkaloid of coffee and tea. Both may be obtained by treating their aqueous infusions (1) with lead acetate to remove extraneous matters; (2) filtering and freeing the filtrate from lead by H_2S; (3) evaporating to dryness and extracting the alkaloid from the residue by absolute alcohol.

They are white, crystalline bodies, of bitter taste, slightly soluble in water, and producing, when swallowed in overdoses, great nervous excitement.

Their use in the common beverages is well known, but it is not so generally recognized that "beef tea" contains bodies so closely related, not only in chemical structure, but in physiological action.

728. **Betaine,** $C_5H_{11}NO_2$, which is found in beet juice ($\frac{1}{4}\%$), is tri-methyl glycocine. When melted with caustic potash it evolves tri-methylamine.

Choline is important because so widely disseminated, being found in many plants as *sincaline;* in the bile (whence its name); in the lecithins (p. 407), and in the brain, as *neurine.* It is a complex *amine* base,

$$(C_2H_4OH) \cdot N(CH_3)_3OH =$$

ethylene hydrate tri-methyl ammonium hydroxide, and may be prepared from white of eggs, or from brains, as a strongly alkaline syrup.

729. **Ox-bile** contains also the sodium salts of two amide-acids. One of these, glycocholic, $C_{26}H_{43}NO_6$, yields, on being boiled with water, cholic acid, $C_{24}H_{40}O_5$, and glycocine; the other, taurocholic acid, $C_{26}H_{45}NSO_7$, yields cholic acid and taurine. Taurine is amid-ethyl-sulphonic-acid $= C_2H_4NH_2 \cdot SO_2OH$. Cholic acid, when mixed with a little sugar, and then with strong H_2SO_4, yields a beautiful purple color. (Pettenkofer's test.)

730. **Leucine** is amid-isocaproic acid,

$$(CH_3)_2 : CH \cdot CH_2 \cdot CH, NH_2 \cdot COOH,$$

and is found in many animal organs, pancreas, brain, etc. It is obtained from gelatin (along with glycocine), and from the albuminoids (along with tyrosine), as a product of putrefaction. The tyrosine is probably an aromatic glycocine, $HO \cdot C_6H_4 \cdot C_2H_3 \cdot NH_2 \cdot COOH$, and is less soluble than leucine.

Leucine crystallizes in pearly plates (sp. gr., 1.3) from its boiling solution in alcohol, and yields, with suitable oxidizing agents, leucic, valeric, and caproic acids.

731. The amides of carbonic acid may be considered as derived from acid ammonium carbonate, $NH_4O \cdot CO \cdot OH$, and normal ammonium carbonate, $NH_4O \cdot CO \cdot ONH_4$. Both of these are found in the commercial *sal-volatile*, as is also a third body, *ammonium carbamate*,

$$NH_2 \cdot CO \cdot ONH_4.$$

This last is also formed by the direct union of dry ammonia, and carbonic anhydride, $2NH_3 + CO_2$.

(1) The *carbamic acid*, $NH_2 \cdot CO \cdot OH$, which it is supposed to contain, is not known in the free state, but it is represented by several salts.

When ammonium carbamate is heated, it breaks up into ammonium carbonate and urea, or carbamide,

$$2(NH_2 \cdot CO \cdot ONH_4) = CO(ONH_4)_2 + CO(NH_2)_2.$$

Carbimide, $CO : NH$, is probably identical with isocyanic acid, $CNOH$. Ammonium isocyanate, $CNONH_4$, when warmed with water, is rapidly converted into its isomer, urea, or carbamide.

(2) *Urea*, $NH_2 \cdot CO \cdot NH_2$, is a product of the final metamorphoses of nitrogenous tissues, and is, therefore, found in the blood, whence it is secreted by the kidneys, and constitutes from 2 to 3% of human urine. A healthy man secretes about 30 grammes of urea daily.

732. Urea may be prepared from human urine (1) by evaporating it to a syrup, cooling, then mixing it slowly with an excess of strong nitric acid. (2) Urea nitrate, $NH_2 \cdot CO \cdot NH_2$, HNO_3, separates out in white masses. (3) This product, after being washed with ice cold water, is purified by recrystallization from hot water. (4) The urea nitrate is now decomposed by barium carbonate,

$$2(NH_2 \cdot CO \cdot NH_2,\ HNO_3) + BaCO_3 = \\ Ba(NO_3)_2 + CO_2 + H_2O + 2(NH_2 \cdot CO \cdot NH_2),$$

the mixture evaporated to dryness; and, finally (5), the urea is extracted by means of strong alcohol.

Urea is the first organic compound artificially prepared, and may be obtained in a state of great purity by boiling an aqueous solution of ammonium isocyanate for a short time (p. 312), then evaporating to dryness, and recrystallizing from its solution in alcohol.

Urea is soluble in water and hot alcohol. Its crystals resemble those of saltpetre in shape, odor and taste. It combines by direct addition with acids and with salts; as, urea hydrochloride, $CO(NH_2)_2HCl$, urea sodium chloride, $CO(NH_2)_2NaCl, H_2O$.

When urea is heated, it melts at 132°C, and is decomposed at 150° into ammonia and a residue containing—

$$\text{biuret} = NH_2CO \cdot NH \cdot CONH_2,$$

and cyanuric acid, $C_3N_3H_3O_3$. On further heating, the cyanuric acid becomes cyanic acid. Urea is also decomposed by long boiling with water, yielding ammonium carbonate, and more readily in the presence of ferments, such as are found in putrefying urine. Dilute solutions of urea when treated with the hypobromites in excess of alkali give the reaction:

$$CO(NH_2)_2 + 3NaBrO + 2NaHO = 3NaBr + H_2O + Na_2CO_3 + \widehat{N_2}.$$

Inasmuch as all the nitrogen escapes in the gaseous form, this reaction may be used as a quantitative test. One gramme of urea should evolve 373CC of free nitrogen.

733. Compound ureas are formed from carbamide by replacing a portion of its hydrogen with alkyl or acid radicals.

(1) The alkyl derivatives are prepared from potassium cyanate by the action of the amine salts. They resemble urea in their general properties; but when boiled with potassium hydrate yield the amines instead of ammonia.

Ethyl urea is $NH_2 \cdot CO \cdot NH \cdot C_2H_5$;

Di-ethyl urea is $C_2H_5 \cdot NH \cdot CO \cdot NH \cdot C_2H_5$,

and its metamer, $NH_2 \cdot CO \cdot N(C_2H_5)_2$. The two first yield ethylamine; the last, di-ethylamine.

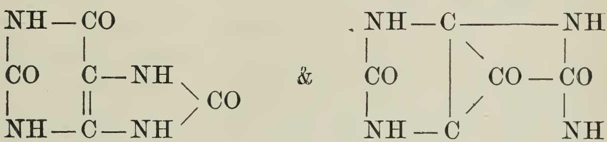
(2) Compound ureas containing a monatomic acid radical are prepared by the action of acid chlorides upon carbamide; thus,

Acetyl-urea, $NH_2 \cdot CO \cdot NHC_2H_3O$, is produced when acetyl chloride is poured upon urea, and forms long silky needles, which are decomposed at high temperatures into acetamide and cyanuric acid.

Compound ureas are also formed by the action of various agents upon uric acid. These contain divalent acid radicals, like—

Oxalyl, $\cdot CO \cdot CO \cdot$;
Mesoxalyl, $\cdot CO \cdot CO \cdot CO \cdot$; and
Tartronyl, $\cdot CO \cdot CHOH \cdot CO$.

734. Uric acid, $C_5H_4N_4O_3$, is a diureide, for which the following structural formulæ have been proposed:



It occurs as urates of soda and ammonia in the urine of all flesh-eating animals, very abundantly in the excrements of serpents. Normal human urine contains about 0.1%, but in some diseases (gout, etc.) it is more abundant, and may form red deposits on standing.

It is prepared from guano (1) by heating with sodium hydrate solution so long as the fumes of NH_3 are given off; and (2), pouring the filtered liquid into dilute hydrochloric acid. Uric acid separates out as a heavy white crystalline powder almost insoluble in cold water and alcohol, but somewhat soluble in strong alkalies. Its lithium salts are characterized by their great solubility.

Uric acid yields a great variety of products when acted upon by oxidizing agents, forming, in alkaline solutions, diureids; as, *uroxanic* acid, $C_5H_8N_4O_6$; *allantoin*, $C_4H_6N_4O_3$. It yields *alloxan*, $C_4H_2N_2O_4$, when digested with strong nitric acid.

735. Alloxan passes by the action of reducing agents to *alloxantin*, $C_8H_4N_4O_7$, $3H_2O$, and to *dialuric acid*, $C_4H_4N_2O_4$. These are converted by the action of ammonia into *dialuramide* or uramil, $C_4H_5N_3O_3$. Various mixtures of these four substances are employed in the manufacture of murexide, which is a valuable red dye-stuff. *Murexide* is the ammonium salt of purpuric acid, $C_8H_4N_5O_6$, NH_4, and crystallizes from its hot solution in gold-green plates. The murexide test for uric acid is very delicate. It is made by dissolving a small quantity of uric acid in nitric acid, evaporating carefully to dryness. The residue, treated with potash, becomes violet; treated with ammonia, purple. Murexide was once used as a purple dye.

736. Hippuric acid, $C_9H_9NO_3$, takes the place of uric acid in the urine of stall-fed horses and cows (1%); and is also found in minute quantity in human urine. It is decomposed by boiling into glycocine and benzoic acid.

$$C_9H_9NO_3 + H_2O = CH_2NH_2 \cdot COOH + C_6H_5COOH.$$

Recapitulation

I.

(1) Any hydrogen atom in NH_3 or in NH_4Cl may be replaced by other radicals.

(2) When alkyl radicals are substituted for hydrogen, an *amine* is formed.

(3) When an acid radical is substituted for hydrogen, an *amide* is formed.

(4) When an alkyl, and also an acid, radical are substituted, an *alkalamide* is formed.

(5) So also the metals may form organo-metallic compounds by the displacement and substitution of the hydrogen in ammonia or ammonium.

(6) The amic acids, or alanines, contain the $(NH_2)'$ group in the alkyl radical and carboxyl, COOH.

(7) The alkalamides have both acid and alkyl radicals, as ethyl-acetamide.

(8) The amines are strong bases, and combine with acids by addition. The primary amides act both as bases and acids; the others generally act as weak acids.

II.

These compounds are *mono* if but one ammonia molecule is so changed; *di* if two, etc., etc. They are *primary* if but one H in the NH_3 molecule is exchanged; *secondary* if two H's are exchanged; *tertiary* if three.

III.

These bodies are of immense importance in both the vegetable and animal kingdoms.

The amines are frequently found in growing plants, as betaine, and are related to some of the alkaloids, as creatine and caffeine. The amides are frequently produced by the decomposition of albumin and gelatin.

The amides of carbonic anhydride form a great number of the products of the decomposition of animal tissues, like urea, uric acid, purpuric acid.

CHAPTER XXV.

THE ETHERS.

737. The term ether is usually employed to include a vast number of substances which agree in containing at least one alkyl radical; as, CH_3I, *methyl iodide;* CH_3CN, *methyl cyanide;* $CH_3 \cdot O \cdot CH_3$, *methyl oxide;* $CH_3 \cdot S \cdot CH_3$, *methyl sulphide;* $CH_3 \cdot O \cdot C_2H_5$, *methyl-ethyl oxide;* and $CH_3 \cdot O \cdot CH_3O$, *methyl formate.* It has been found possible to classify these in groups, like the four already defined upon page 298.

I. Haloid ethers, including the cyanides.
II. Simple ethers, the oxides, sulphides, etc.
III. Mixed ethers, with two different alkyl radicals.
IV. Ethereal salts, containing also an acid radical.

738. The haloid ethers, containing chlorine and bromine, may be prepared by the direct action of these elements in the sunlight upon the paraffins; as,

$$CH_4 + Cl_2 = HCl + CH_3Cl.$$

Usually, all are obtained from the anhydrous alcohols by the action of the haloid compounds of phosphorus; as, $CH_3OH + PBr_5 = HBr + POBr_3 + CH_3Br$. More frequently in the case of bromine and iodine by a mixture of these elements with phosphorus; as,

$$4CH_3OH + I_5 + P = PO(OH)_3 + HI + 4CH_3I.$$

Each alkyl radical may have a full series of chlorides, bromides, iodides, and cyanides. By far the greater

number are of interest only as items necessary to render such series complete. They are generally colorless liquids, freely soluble in alcohol, and but slightly in water. The lower members volatilize readily, yielding vapors of characteristic odors, which are often fragrant and usually exceedingly inflammable.

They are very susceptible to chemical change, and are of great use in synthetical operations (especially the iodides), as is exhibited by the following general reactions of the haloid ethers:

I. With nascent hydrogen = the paraffins; as,
$$CH_3Cl + HCl + Zn = ZnCl_2 + CH_4.$$

II. With metallic zinc = the organo-base; as,
$$2CH_3Cl + 2Zn = ZnCl_2 + (CH_3)_2Zn.$$

III. With ammonia = the amines; as,
$$CH_3I + NH_3 = HI + CH_3NH_2.$$

IV. With NaHO or AgHO = the alcohols; as,
$$CH_3I + AgHO = AgI + CH_3OH.$$

V. With sodium alcoholate = the ethers; as,
$$CH_3I + CH_3ONa = NaI + CH_3 \cdot O \cdot CH_3.$$

VI. With silver salts of the organic acids = the ethereal salts; as, $CH_3I + H.COOAg = AgI + CH_3 \cdot O \cdot CHO.$

VII. With potassium cyanide = the cyanides; as,
$$CH_3I + KCN = KI + CH_3CN.$$

VIII. With KCNS = the sulpho-cyanates; as,
$$CH_3I + KCNS = KI + CH_3CNS.$$

IX. With KHS = the mercaptans; as,
$$CH_3I + KHS = KI + CH_3SH.$$

739. Methyl chloride, CH_3Cl, is easily prepared by heating together methyl alcohol, common salt, and strong sulphuric acid. It is a gas which may be liquefied at —22°C. By the action of chlorine in sunlight, it yields in succession, CH_2Cl_2, *methene chloride;* $CHCl_3$, *methenyl chloride;* and CCl_4, *carbon tetrachloride.*

740. Chloroform, $CHCl_3$, is usually prepared from alcohol. This is mixed with 32 parts of water and 10 parts of chloride of lime; heated quickly until the reaction begins and then distilled. The chloroform passes over with the first portions, mixed with water, but soon settles out by reason of its insolubility in water. The crude choloform is purified by washing with water and by redistillation.

Chloroform is a colorless liquid of sweetish taste and pleasant odor; density, 1.525; boils at 63.5°C. It burns with a greenish flame, but is not easily ignited. It is remarkable for its anæsthetic powers, its vapors, when inhaled, speedily producing insensibility to pain. It is also an excellent solvent for many resins and alkaloids, and for Br, I, P, etc.

When boiled with an alcoholic solution of caustic potash, it is converted to potassium formate,

$$CHCl_3 + 4KHO = 2H_2O + 3KCl + H, COOK;$$

but if ammonia is at the same time present, potassium cyanide is formed, $CHCl_3 + NH_3 + 4KHO = 4H_2O + 3KCl + KCN$. When boiled with chlorine in the sunlight it yields carbon tetrachloride, CCl_4, a colorless liquid of ethereal odor; density, 1.56; boils at 78°C. Nascent hydrogen changes CCl_4 by retrograde steps into $CHCl_3$, CH_2Cl_2, CH_3Cl, and to CH_4.

741. Bromoform, $CHBr_3$, and *iodoform*, CHI_3, are obtained by heating an alcoholic solution of caustic potash with bromine or iodine, avoiding excess. Bromoform is a liquid which resembles chloroform, but has almost double the density (2.9), and a higher boiling point (152°C).

Iodoform crystallizes in yellow leaflets, which smell like saffron. It is used in medicine in place of free iodine (see page 324).

742. Ethyl chloride, CH_5Cl, is prepared by saturating

cold absolute alcohol with dry hydrochloric acid gas. After standing some days in stoppered vessels, the product is distilled upon a water-bath, and the vapors condensed in a receiver, surrounded by ice and salt. It is an extremely volatile liquid; sp. gr., 0.92; boiling point, 12°C. With chlorine, in sunlight, it yields all the other chlorides of the ethyl radical,

$$C_2H_4Cl_2,\ C_2H_3Cl_3,\ C_2H_2Cl_4,\ C_2HCl_5, \text{ and } C_2Cl_6.$$

The first of these is $CH_3 \cdot CHCl_2$, *ethylidene chloride*, a fragrant liquid boiling at 60°, which may be supposed to contain the radical $(CH_3 \cdot CH)''$, or ethylidene. It is isomeric with the following:

Ethylene chloride, $ClH_2C \cdot CH_2Cl$, was long known under the name, Dutch liquid. When pure, it is a thin liquid, of sweetish taste, and an odor resembling chloroform; boils at 85°C; density, 1.27. It is prepared by mixing equal volumes of dried chlorine and olefiant gas in a capacious globe (see Fig. 106). The combination takes place rapidly, and the product trickles down into a cooled receiver, which should be provided with an escape pipe for any uncondensed gases. This crude product is washed with water, dried by strong sulphuric acid, and redistilled.

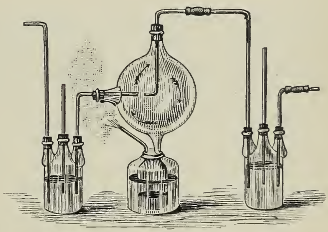


FIG. 106.

A large number of chlorides may be obtained from this by successive treatment: (1) with potassium hydroxide, which removes one chlorine atom; as, $C_2H_4Cl_2+KOH=KCl+H_2O+C_2H_3Cl$; and then (2), with chlorine, which again adds two ($C_2H_3Cl_3$). These products, together with those formed from ethane or ethyl chloride, are given in the following table, together with their boiling points. It will be noticed that there are three pairs of isomers. The table

is an illustration of the variety of compounds which may be produced by chlorine, bromine, and iodine upon the hydrocarbons and their alcoholic derivatives. Compounds are also known which contain two haloids; as, chlor-iod-ethylene, $CH_2Cl \cdot CH_2I$.

From Ethylene.		From Ethane.
By Substitution.	By Addition.	
Ethylene, CH_2, boiling pt. ‖ —110°. CH_2.	Ethylene di-chloride. CH_2Cl, boiling pt. | 85°. CH_2Cl.	Ethyl chloride, CH_3, boiling pt. | 12°. CH_2Cl.
Chlor ethylene, CH_2, boiling pt. ‖ —18°. $CHCl$.	Chlor ethylene di-chloride, CH_2Cl, boiling pt. | 115°. $CHCl_2$.	Di-chlor ethane, CH_3, boiling pt. | 59°. $CHCl_2$.
Di-chlor ethylene, $CHCl$, boiling pt. ‖ 37°. $CHCl$.	Di-chlor ethylene di-chloride, $CHCl_2$, boiling pt. | 137°. $CHCl_2$.	Tri-chlor ethane, CH_3, boiling pt. | 75°. CCl_3.
		Tetra-chlor ethane, CH_2Cl, boiling pt. | 102° CCl_3.
Tri-chlor ethylene, $CHCl$, boiling pt. ‖ 88°. CCl_2.		Penta-chlor ethane, $CHCl_2$, boiling pt. | 158°. CCl_3.
Tetra-chlor ethylene, CCl_2, boiling pt. | 117°. CCl_2.		Per-chlor ethane, CCl_3, boiling pt. | 182°. CCl_3.

743. The halogen compounds of the higher carbon nuclei increase theoretically very rapidly. Only a small part of these are known, and few of these of practical importance.

For example, the three carbon nucleus includes such bodies as *propane*, C_3H_8; *propene*, C_3H_6; *allylene*, C_3H_4, and their alcohols *propyl*, *isopropyl*, C_3H_7OH; *propyl glycol*, $C_3H_6(OH)_2$, and *glycerol*, $C_3H_5(OH)_3$, each with its own series of derivatives.

Of these, *allyl iodide*, C_3H_5I or $CH_2:CH \cdot CH_2I$, may be prepared by heating glycerol with phosphorus and iodine. It is an oily liquid smelling strongly like leeks. From it may be obtained *allyl alcohol*, C_3H_5OH, and other interesting derivatives, as the artificial mustard oils and some of the "hydrins."

744. The term hydrin ought to be restricted to those halogen ethers of the polyhydric alcohols which still contain hydroxyl, but it is somewhat loosely applied, especially in case of the halogen ethers of glycerol.

If the glycols or the glycerols be saturated with dry hydrochloric acid gas, the mixture digested for some time at a moderate heat and then distilled, a portion of the hydroxyl of these alcohols will be replaced by chlorine; as, glycol mono-chlor-hydrin, $CH_2Cl \cdot CH_2OH$, and with glycerin, chlorhydrin, $C_3H_5Cl(OH)_2$, and di-chlorhydrin, $C_3H_5Cl_2OH$. Isomers of the two latter may be formed from allyl iodide. All these are thin, colorless liquids of somewhat lower boiling point than the alcohols from which they are formed. By the aid of phosphorus penta-chloride, the last hydroxyl may be displaced, forming, for example, glycol di-chloride, $CH_2Cl \cdot CH_2Cl$, and tri-chlorhydrin, $C_3H_5Cl_3$, which boils at 158°C; sp. gr. 1.42.

Epichlorhydrin, C_3H_5OCl, which still more closely resembles chloroform (boils 118°; sp. gr., 1.19) is prepared by mixing the di-chlorhydrins with strong caustic alkali, and shaking:

$$C_3H_5Cl_2OH + KOH = KCl + H_2O + C_3H_5OCl.$$

745. The nitro paraffins are formed when silver nitrite is added to the alkyl iodides; as, $C_2H_5 \cdot I + AgNO_2 = AgI + C_2H_5NO_2 =$ nitro ethane. The action is violent,

and much heat is given out. Sometimes the isomeric nitrous ethers, as $C_2H_5 \cdot O \cdot NO$ = ethyl nitrite, are produced at the same time, but these are of far lower boiling point, and are easily separated by fractional distillation. The nitro paraffins are oily liquids, quite stable, but capable of forming compounds that are fearfully explosive; as, $C_2H_4NaNO_2$.

Any nitro-derivative, when treated with nascent hydrogen, is converted to its *amine;* as, $C_2H_5NO_2 + H_6 = 2H_2O + C_2H_5NH_2$ = *ethyl amine*, which seems to indicate that the nitrogen in it is directly united to the carbon nucleus. Those of the "closed chain" series are of great use in synthetical chemistry; but those of the "open chain" are of little importance.

746. The normal cyanogen ethers are identical with the nitrils (§ 723), and are characterized by the readiness with which they exchange the cyanogen for the carboxyl group; as, in the reaction with potassium hydroxide, $CH_3 \cdot CN + KHO + H_2O = NH_3 + CH_3 \cdot COOK$.

It will be noticed that the acid thus formed has one carbon atom more than the alcohol from which it came. By taking advantage of this fact, and of the fact that any acid may be reduced to its corresponding alcohol, all of the alcohols in a given series may be obtained from the first; viz, by forming in succession (1) the cyanogen ether, (2) the acid salt, (3) the acid of higher carbon content, (4) the alcohol corresponding.

Only the first five of the alkyl isocyanides are known. In these the nitrogen is penta valent, as in *methyl isocyanide*, $CH_3 \cdot N \vdots C$, the alkyl radical being directly united to the nitrogen. With potassium hydroxide, they yield small quantities of potassium formate, and the amine of the alkyl radical, instead of the NH_3; for example, $CH_3 \cdot N \vdots C + KHO + H_2O = H \cdot COOK + CH_3 \cdot NH_2$. Acids easily convert them to formic acid and an amine salt.

747. The simple ethers may be prepared by heating a sodium alcoholate with an alkyl iodide; as,

$$CH_3ONa + CH_3I = NaI + CH_3 \cdot O \cdot CH_3 = \text{methyl ether.}$$

Mixed ethers are formed when two different alkyl radicals enter into the reaction; as, $CH_3ONa + C_2H_5I = NaI + CH_3 \cdot O \cdot C_2H_5$ = methyl-ethyl ether.

The usual process for making the simple ethers consists in heating the respective alcohols with strong sul-

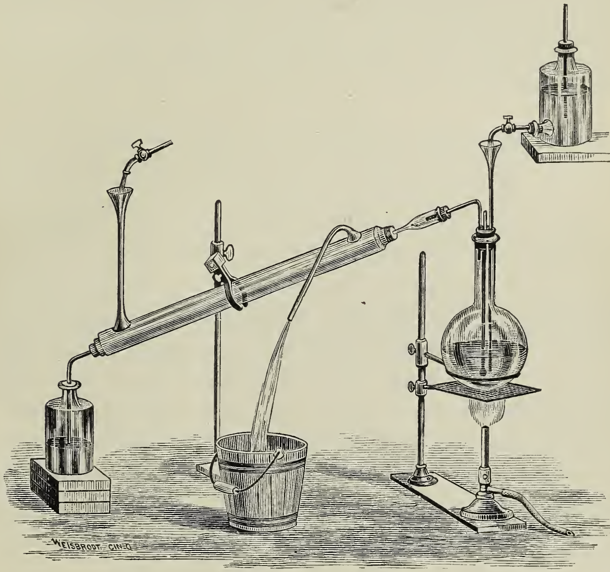


FIG. 107.

phuric acid. The reactions which take place in the use of ethyl alcohol have been given on page 322. The temperature required to produce ethyl ether by the decomposition of the monoethylic sulphate is about 140°C. The regenerated sulphuric acid is of course in condition to act upon fresh molecules of the alcohol. The process is made *continuous* by starting with a mixture that boils at the required temperature, say five parts of strong alcohol with nine parts of strong sulphuric acid.

Fig. 107 exhibits a convenient apparatus. A flask is provided with a stopper having three holes; one for a thermometer, one for the supply of alcohol, and the last for the escape of the vapors into the condenser. As soon as the liquid begins to distil at 140°C, the alcohol is allowed to enter at the bottom of the flask at such a rate that a nearly uniform temperature is maintained. In practice, there is always a little waste, other organic products are formed, and sulphurous acid evolved; the distillate also contains unaltered alcohol and water. The ether is purified: (1) by agitation with milk of lime; (2) drying with calcium chloride; and (3), redistillation.

748. Ethyl ether, $(C_2H_5)_2O$, is sold under the name of sulphuric ether. It is a colorless fluid of pleasant odor, so named ethereal; boiling at 35°C; sp. gr. 0.74. It mixes with alcohol in all proportions; with water only to about one tenth the weight of each. It is a solvent for the fats, resins, many other organic bodies, and, to a much less degree, for sulphur and phosphorus. Owing to its ready volatility it is used for the production of cold, but its use requires care, as its vapor is very easily set on fire, and, when mixed with air, becomes violently explosive. The vapor when inhaled produces complete insensibility to pain, and is the chief anæsthetic used by surgeons in the United States. Swallowed, it has a fiery taste, and, even in small doses, rapidly brings on the stupor of intoxication.

749. Methyl ether, $CH_3 \cdot O \cdot CH_3$, is made from methyl alcohol and strong sulphuric acid. It is a colorless gas, combustible, condensed by a cold of —21° to a liquid. Cold water absorbs 37 times its volume, and acquires thereby the taste and odor of the ether. It is metameric with ethyl alcohol, $CH_3 \cdot CH_2OH$.

750. Methyl-ethyl ether, $CH_3 \cdot O \cdot C_2H_5$, is formed by the metathesis of sodium ethylate and methyl iodide. It is an inflammable liquid, boiling at 11°, and resembling ethyl ether in most other particulars.

Three ethers are known which are metameric with butyl alcohol, $C_4H_{10}O$, and six with amylic, $C_5H_{12}O$.

Allyl alcohol, C_3H_5OH, has also its ethers, which are formed from allyl iodide, C_3H_5I. The following is the reaction for allyl ether, $2C_3H_5I + Ag_2O = 2AgI + (C_3H_5)_2O$. It is a colorless liquid, boiling at 82°. It is thought to exist free in the crude oil of garlic, together with the ethereal sulphide, $(C_3H_5)_2S$.

Mixed allyl ethers result by treating these with sodium alcoholates; as, $C_3H_5I + CH_3ONa = NaI + C_3H_5 \cdot O \cdot CH_3$, yields allylmethyl ether. The general behavior of these compounds is quite analogous to those previously described.

The oxides of the glycols are produced by the action of caustic potash upon their chlorhydrins; as, $CH_2Cl \cdot CH_2OH + KOH = KCl + H_2O + CH_2 \cdot O \cdot CH_2$ = ethylene oxide.

Ethylene oxide, C_2H_4O, is a liquid of pleasant odor; sp. gr., .898; boils at 13.5°; a strong base combining with acids to form compound ethylene ethers.

A glyceryl oxide also exists, $(C_3H_5)_2O_3$, which remains along with allylin, $C_3H_5(OH)_2 \cdot O \cdot C_3H_5$, in the retorts used in making allyl alcohol by heating glycerine with oxalic acid.

751. Thio ethers may be obtained by heating the alkyl chlorides with an alcoholic solution of potassium sulphide and distilling; as,

$$2C_2H_5Cl + K_2S = 2KCl + (C_2H_5)_2S = \text{ethyl sulphide.}$$

These bodies are for the most part liquids, easily volatilized, and of an offensive odor, which is frequently characteristic. They bear the same relation to the mercaptans that oxygen ethers do to the alcohols.

Allyl sulphide, $(C_3H_5)_2S$, is the most interesting of these, as it is the principal part of the oil obtained by distilling garlic with water. It is formed synthetically from allyl iodide, $2C_3H_5I + K_2S = 2KI + (C_3H_5)_2S$.

752. Allyl sulphocyanate, $C_3H_5 \cdot CNS$, is obtained (synthetically) from the reaction,

$$C_3H_5I + KCNS = KI + C_3H_5 \cdot CNS,$$

and also from black mustard-seeds. These seeds contain a bland oil, which may be removed by pressure. (2) The "oil-cake" remaining contains potassium myronate, and a natural ferment called *myrosin*. Upon the addition of water, a fermentation is set up, and the potassium myronate is converted into glucose, acid potassium sulphate, and the allyl mustard-oil, $C_{10}H_{18}KNS_2O_{10} = C_6H_{12}O_6 + KHSO_4 + C_3H_5CNS$. The mustard-oil is then distilled by the aid of steam; sp. gr., 1.02; boils, 150°C. It blisters the skin quickly, and its vapors are exceedingly pungent.

The term "mustard-oils" is made also to include other isosulphocyanates (as C_2H_5CNS = ethyl sulphocyanate), which have some of the properties of the allyl-oil.

Selenium and tellurium also act as "linking elements" between two alkyl radicals. The ethers they form have as a rule exceedingly enduring and offensive odors.

753. The compound ethers are ETHEREAL SALTS, which exactly correspond to the metallic salts of the oxy-acids. A great variety of these compounds are known, inasmuch as any acid radical may be made to combine with any alkyl radical of equal valency to produce them.

Some one of these compounds is always formed when the alcohols and strong acids are mixed together; as, $C_2H_5OH + HNO_3 = H_2O + C_2H_5 \cdot ONO_2$ = ethyl nitrate = nitric ether. With polybasic acids several ethereal salts may be formed; as, C_2H_5, H_2PO_4, monethyl phosphate; $(C_2H_5)_2HPO_4$, di-ethyl phosphate, which are *ether acids*, and $(C_2H_5)_3PO_4$, tri-ethyl phosphate, which is a neutral ether.

All compound ethers are reconverted by heated steam into free acid and free alcohol; or, more simply, by boiling with a strong base, like caustic soda or lime; as, $C_2H_5 \cdot ONO_2 + NaOH = NaNO_3 + C_2H_5OH$. This process is known as saponification.

754. The nitric ethers are prepared in small quantities and at low temperatures. Ethyl nitrate, $C_2H_5ONO_2$, is obtained by distilling 60 grammes of alcohol with an equal weight of strong nitric acid, 15 grammes of urea being previously added. The ether is nearly insoluble in water, and may be freed from the alcohol, which distils over with it, by washing with water and rectifying with $CaCl_2$. It is a colorless liquid of agreeable odor; sp. gr., 1.11; boils at 85°. Its vapor, when overheated, is explosive.

Ethyl nitrite, C_2H_5ONO, is obtained pure by passing the vapors of nitrous anhydride into alcohol, kept cool by ice, $2C_2H_5OH + N_2O_3 = H_2O + 2C_2H_5ONO$. It is a colorless liquid, having the odor of apples; sp. gr., 0.95; boils at 16°; soluble in 40 parts of water. The "*sweet spirits of nitre*" is a solution of ethyl nitrite in alcohol, mixed with oxidation products,—aldehyde, acetic acid, ethyl acetate, etc., which are sometimes present in sufficient quantity to render it unfit for use.

755. It has already been noted that sulphuric acid forms two series of ethereal salts. For example: ethyl sulphate, $(C_2H_5O)_2SO_2$, formed by passing the vapor of SO_3 into well cooled anhydrous ether, and sulphovinic or ethyl sulphuric acid, $C_2H_5O \cdot SO_2 \cdot OH$, which is an intermediate product in the manufacture of ether.

This may be isolated (1) by digesting a mixture of three molecules of alcohol with one of the strong acid. (2) Diluting the mixture with water and saturating with lead carbonate. (3) Filtering off the lead salt, and decomposing it with H_2S. (4) The free acid is then concentrated to an acid syrup; sp. gr., 1.3. Unlike sulphuric acid, all its salts are soluble in water. It is easily decomposed on heating, and if heated with ethyl alcohol yields ethyl ether; with other alcohols, the mixed ethers. For example: with amyl alcohol, ethyl amyl ether,

$$C_2H_5O \cdot SO_2 \cdot OH + C_5H_{11} \cdot OH = H_2SO_4 + C_2H_5 \cdot O \cdot C_5H_{11}.$$

756. Ethyl sulphite, $C_2H_5O \cdot SO \cdot C_2H_5O$, is formed by the action of sulphur-di-chloride upon alcohol; as,

$$3(C_2H_5OH) + S_2Cl_2 = 2HCl + C_2H_5SH + (C_2H_5O)_2SO.$$

It is a liquid of peppermint-like odor; sp. gr., 1.08; boils, 160°. No acid sulphites corresponding to these are known, but instead of them an important series of isomers which may be considered as derived from an unsymmetrical sulphurous acid, $H \cdot SO_2 \cdot OH$, and which take the name of *sulphonic acids.* The sulphonic acids may be formed by oxidizing the mercaptans; as,

$$C_2H_5SH + O_3 = C_2H_5SO_2OH = \text{ethyl sulphonic acid, or}$$

by heating the haloid ethers with potassium sulphite; as,

$$C_2H_5I + K_2SO_3 = KI + C_2H_5SO_2OK = \text{potassium ethyl sulphonate.}$$

These acids are stable compounds, in every way analogous to the carboxyl acids. Their ethers are formed by the action of their chlorides upon sodium alcoholates; as, $C_2H_5 \cdot SO_2 \cdot Cl + C_2H_5ONa = NaCl + C_2H_5SO_2 \cdot O \cdot C_2H_5 =$ ethylic ethyl-sulphonic ether.

757. The ethereal salts of the organic acids are usually prepared by heating the respective alcohols with a mixture of the sodium salt of the acid and strong sulphuric acid.

Sulphuric acid is commonly used in the manufacture of the oxygen ethereal salts; partly because of its reactions with the alcohols, and partly because it serves to liberate from their salts other acids that they may act in a nascent state upon the alcohols; as, $2(CH_3COONa) + H_2SO_4 = Na_2SO_4 + 2(CH_3COOH)$.

$C_3H_6O_2$. Methyl acetate, $CH_3 \cdot O \cdot C_2H_3O$, occurs in crude wood spirit; sp. gr., .956; boils, 56°C. Its isomer, ethyl formate, $C_2H_5 \cdot O \cdot CHO$, is prepared by digesting oxalic acid, glycerine, and alcohol and afterwards distilling. It is a liquid, having an odor recalling that of peach kernels; sp. gr., .945; boils, 54°C.

$C_4H_8O_2$. Ethyl acetate, $C_2H_5 \cdot O \cdot C_2H_3O$, is obtained by distilling one part of alcohol with two parts of sodium acetate, and three parts of sulphuric acid. The crude product is washed with a very little strong brine, and rectified over calcium chloride. It is a colorless liquid, of an agreeable ethereal odor; sp. gr., 0.9; boils, 73°; soluble in 17 parts of water, and partially decomposing in it. Its metamers are propionic formate, $C_3H_7 \cdot O \cdot CHO$; the methyl propionates, $CH_3 \cdot O \cdot C_3H_5O$; and the butyric acids, $C_3H_7 \cdot COOH$.

758. Many of the ethereal salts, which are analogous to these, have agreeable odors, which, in some cases, resemble those of fruits; ethyl butyrate, that of pine apples; isoamyl acetate, that of jargonelle pears; isoamyl isovalerate, that of apples; ethyl pelargonate, that of quinces. Ethyl œnanthate is thought to be a part of the aroma of old wines.

The artificial fruit essences are mixtures of such ethers, with acetic ether, alcohol, and glycerine. The mixtures used in the compounding of imitation spirits are of the same sort, rum essence contains ethyl formate, etc., cognac essence, acetic and nitrous ethers, etc. Some of the odoriferous oils, naturally occurring in plants and in animals, are also ethereal salts, as the oil of wintergreen is, $CH_3 \cdot O \cdot C_7H_5O_2$ = methyl salicylate. Such are also spermaceti and the chief constituents of bees-wax.

The ethereal salts of polyvalent radicals (acid as well as alkyl) are of almost infinite variety. The oxygen ethers of carbonic acid should be two; as, ethyl carbonate, $C_2H_5O \cdot CO \cdot OC_2H_5$, obtained by metathesis of silver carbonate and ethyl iodide, and acid ethyl carbonate, $C_2H_5O \cdot CO \cdot OH$, which is known only in its salts, such as ethyl potassium carbonate, $C_2H_5O \cdot CO \cdot OK$, obtained by passing carbonic anhydride into an alcoholic solution of caustic potash. The *fats* are salts of glycerol, §646.

Thio-carbonic ethers are formed from the alkyl iodides by the action of the alkaline sulpho-carbonates; as, $2C_2H_5I + K_2S, CS_2 = 2KI + (C_2H_5S)_2CS$ = ethyl sulpho-carbonate.

The best known of the acid thio ethers are the xanthates, which are ethyl di-thio-carbonates. Potassium xanthate is prepared by mixing a saturated solution of caustic potash in hot alcohol with carbon bisulphide, $CS_2 + KHO + C_2H_5OH = H_2O + C_2H_5 \cdot O \cdot CS \cdot SK$, which separates out on cooling in beautiful silky needles; sp. gr., 1.56. These must be quickly dried and kept out of contact with the air. It is a very delicate test for cupric salts, which yield, with it in aqueous solutions, yellow cuprous xanthate $(C_2H_5O \cdot CS \cdot S)_2Cu_2''$.

Potassium xanthate, when decomposed by cold dilute sulphuric acid, yields xanthic acid, $C_2H_5O \cdot CS \cdot SH$, a colorless, oily liquid, heavier than water, and decomposed at 24° into alcohol and carbonic bisulphide. It is proposed to use this body, and some of its compounds in place of CS_2 for destroying insects on plants and in grain. Like any other acid, it has its metallic salts, ethers, etc., $C_2H_5O \cdot CS \cdot SC_2H_5 =$ xanthic ether, amides, $C_2H_5O \cdot CS \cdot NH_2 =$ xanthamide, and other derivatives.

The thio compounds of other alcohol radicals, as far as known, agree with those described.

759. The normal oxalic ethers are prepared by digesting oxalic acid with the anhydrous alcohols, and afterwards distilling. The acid ethers are little known in the free state.

Ethyl oxalate, $C_2H_5O \cdot CO \cdot CO \cdot OC_2H_5$, is a colorless liquid, of faint odor; sp. gr., 1.08; boils, 186°. It is very easily decomposed, and is converted by dry gaseous ammonia into ethyl oxamate, $C_2H_5O \cdot CO \cdot CONH_2$, and by aqueous ammonia into oxamide, $NH_2CO \cdot CONH_2$, and alcohol.

The polyhydric acids are capable of forming ethers by the substitution of an alkyl radical for their replaceable hydrogen. If their basic hydrogen be wholly replaced, they yield *normal* ethereal salts; and if partially replaced, *acid* salts, as illustrated by those of tartaric acid on the next page. If the normal salts are treated with the chlorides of acid radicals, even the alcoholic hydrogen may be replaced by such acid radicals, as in ethyl di-acetotartrate, $(CH)_2(OC_2H_3O)_2(COC_2H_5)_2$.

Tartaric acid.	Acid ethyl tartrate.	Normal ethyl tartrate.
COOH	$COOC_2H_5$	$COOC_2H_5$
|	|	|
CHOH	CHOH	CHOH.
|	|	|
CHOH	CHOH	CHOH.
|	|	|
COOH	COOH	$COOC_2H_5$.

So also the amid-acids have their ethers, as the ethyl amid-acetate, $CH_2NH_2 \cdot COOC_2H_5$, obtained from glycocine.

Enough has been given to illustrate the wonderful flexibility of organic compounds, and to indicate the methods by which they are obtained and classified. Each radical has, so to speak, its own personality, and, so long as it exists entire, plays a definite part in the various compounds into which it enters. When, however, it is modified by becoming chlorinated, oxidized, etc., it forms a new group with new functions. The ethers are the best illustrations of these growths and transformations.

760. The lecithins are a group of complex ethers of glycerol, found in the cell substance of maize, brain substance, egg, albumin, etc. They are fats containing the radicals of two fatty acids, glycerol, phosphoric acid, and the ammonium hydroxide, *neurine* (p. 386). The brain substance probably contains palmitic-oleic lecithin.

$$\begin{array}{l} CH_2 \cdot O \cdot C_{16}H_{31}O. \\ | \\ CH \cdot O \cdot C_{18}H_{33}O. \\ | \\ CH_2 \cdot O \cdot PO \cdot OH. \\ \qquad\qquad\quad O \cdot (C_2H_4)N(CH_3)_3OH. \end{array}$$

Recapitulation.

(1) The ethers are volatile, inflammable compounds of characteristic odors.

(2) Each contains at least one alkyl radical united to a negative radical, like I', or O'', or P'''.

(3) Haloid ethers contain only one alkyl radical.

(4) Simple ethers contain two or more similar alkyl radicals united by O, by S, etc.

(5) Mixed ethers contain two or more dissimilar alkyl radicals.

(6) Compound ethers contain an acid radical, and are *ethereal salts.*

(7) These ethers are easily broken up, and are, therefore, useful in chemical synthesis.

(8) The conversion of the ethereal salts into their alcohols and acids is known as saponification. It may be accomplished by heating with steam, with alkalies, and with acids.

(9) The hydrins are ethers formed from polyhydric alcohols by the substitution of negative radicals for a part or the whole of their hydroxyl.

(10) The compounds of nitrogen, with alkyl radicals, are of two sorts; ethereal salts, like the nitric and nitrous ethers; and the nitro derivatives, which yield amines with nascent hydrogen.

(11) The cyanogen compounds are also two, — cyanides and isocyanides.

CHAPTER XXVI.

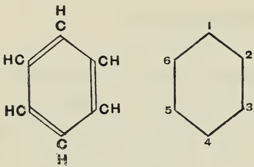
THE AROMATIC HYDROCARBONS.

761. The aromatic hydrocarbons may be regarded as derived from BENZENE, C_6H_6, by successive additions of CH_2, or by conjugation of two or more benzene molecules. The six hydrogen atoms of benzene may, one after the other, be replaced by monovalent radicals, like Cl, OH, COOH. It is noticeable that the "nitro," NO_2, substitution takes place more readily than is the case with the fatty derivatives, generally by direct action of strong nitric acid, and not requiring the previous formation of chlorides, etc.; and also that strong sulphuric acid readily forms with them the *sulphonic acids*, containing the group SO_2OH, and that these two classes of derivatives are of much greater importance than the analogous compounds in the fatty series.

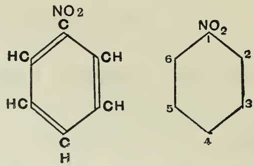
Although most of the derivatives known contain one, two, or three substitutions of hydrogen; it appears that all of the hydrogen atoms in benzene have the same value, as if the empirical formula of benzene were $(CH)_6$. Consequently, substances like C_6H_5Cl or $C_6H_5NO_2$, in which only a single hydrogen atom has been replaced by a monovalent radical, can have no true isomers; their metamers, if any, must come from the fatty series.

762. These facts have led to the theory that in the benzene group, C_6H_6, (1) the six carbon atoms, which constitute the "benzene nucleus," are so united as to form a "closed chain," and to leave one valency free for each. (2) That this valency is satisfied in benzene

by hydrogen; (3) that "substitution products" are formed by the replacement of these hydrogen atoms by other radicals. These notions find expression in the diagrams already given on page 289, or more simply by a hexagon with angles numbered to represent the places of the six CH groups, or their substitution products:

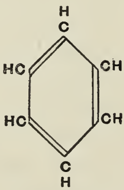


C_6H_6, benzene.

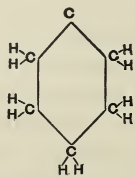


$C_6H_5NO_2$, nitro-benzene.

(4) A very few "addition products" are known, as $C_6H_6H_6$ and $C_6H_6Cl_6$. In such compounds each carbon atom must act divalent, and consequently the chain must be unlocked.



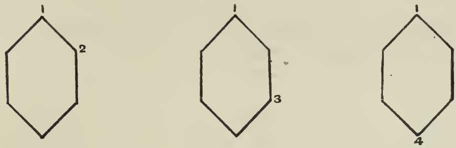
Benzene.



Hexa-hydro-benzene.

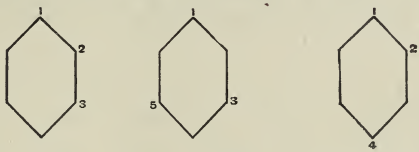
763. Compounds formed by the substitution of two or more hydrogen atoms exhibit, in a marked degree, the isomerism which is due to the *position* or *orientation* of the substituted radicals. There are three cases of such isomerism due to *two* substitutions: (1) *Ortho* derivatives are formed by consecutive substitution, displacing neighboring carbon atoms, as 1:2 or 2:3, etc. (2) *Meta* derivatives, by substitutions separated by a single hydrogen

atom, as 1:3 or 1:5. (3) *Para* derivatives, by substitution as widely separated as possible; viz, 1:4:



Ortho. Meta. Para.

Three isomers are also possible when the same radicals are substituted *three* or *four* times for as many hydrogen atoms. These are designated as



Consecutive. Symmetrical. Unsymmetrical.

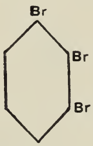
according to the positions which the substituted radicals take, as illustrated by the diagrams.

The position which is assigned to any group is determined by the compounds into which it enters, or from which it may be derived. A *para* compound can come only from an unsymmetrical tri-derivative; an *ortho* from either an unsymmetrical or consecutive tri-derivative, and a *meta* from any one of the three tri-derivatives. Hence, this rule.

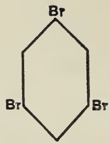
The di-derivatives of benzene are termed para (1:4), *ortho* (1:2), *and meta* (1:3), *according as they may be formed from or give rise to one, or two, or three tri-derivatives.*

764. When the substituted radicals are different, the number of isomers is greatly increased, and also the difficulty of establishing their orientation.

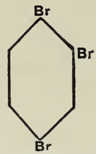
For example, the trivalent, C_6H_3, is the nucleus for three tribrom derivatives, $C_6H_3Br_3$; viz,



Consecutive.

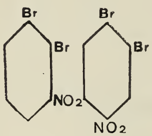


Symmetrical.

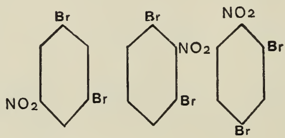


Unsymmetrical.

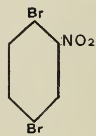
Now, if one of these be replaced by the radical nitryl, NO_2, six isomers of nitro-di-brom benzene, $C_6H_3Br_2NO_2$, become possible; viz,



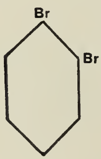
Yielding ortho di-brom benzene.

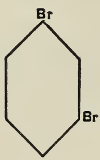


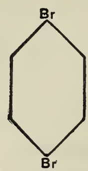
Yielding meta di-brom benzene.



Yielding para di-brom benzene.

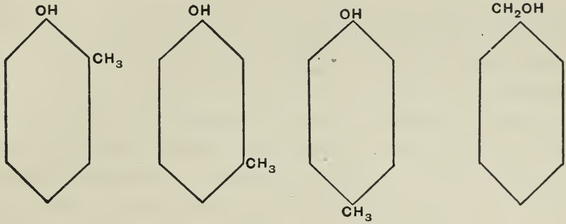






765. Another kind of isomerism is caused by parallel substitutions; one in the nucleus, and another in the

lateral chain. The three cresols, $C_6H_4 \cdot OH$, CH_3, are metameric with benzyl alcohol. $C_6H_5 \cdot CH_2OH$.



Ortho. Meta. Para. Primary

Cresols, C_7H_8O. Benzyl alcohol, C_7H_8O.

Similarly, chlorine, when passed *into boiling toluene*, $C_6H_5 \cdot CH_3$, produces a series of chlorides, which are very like the chlorides of the alcohols. This substitution is supposed to take place in the lateral chain, as benzyl chloride, $C_6H_5 \cdot CH_2Cl$; benzyl di-chloride, $C_6H_5 \cdot CHCl_2$, and benzyl chloroform, $C_6H_5 \cdot CCl_3$.

Very different compounds are formed when the reaction takes place *in the cold* or in the presence of iodine, the substitution then taking place in the nucleus, as chlor-toluene, $C_6H_4Cl \cdot CH_3$; di-chlor-toluene, $C_6H_3Cl_2 \cdot CH_3$, etc., to $C_6Cl_5 \cdot CH_3$, and there are also chlorides containing both kinds of substitutions; as,

$$C_6H_4Cl \cdot CH_2Cl = \text{chlor-benzyl chloride},$$

metameric with the other two di-chlorides. Altogether, there are nearly a hundred chlorides between $C_6H_5 \cdot CH_3$ and $C_6Cl_5 \cdot CCl_3$.

766. Many of the aromatic hydrocarbons are obtained by the fractional distillation of coal-tar, which is a bye-product in the manufacture of illuminating gas. The first portion (about 10% of the tar) is *light oil*, which is a mixture of hydrocarbons lighter than water, as *benzene*, *toluene*, etc. The second portion (about 25%) is the *heavy* or *dead* oil which contains the *phenols*, the *amine* bases, and *naphthaline*. (3) If the *pitch* which

remains is further distilled, solid hydrocarbons, like *anthracene* and *chrysene*, pass over; and (4), there remains as a final product only a residue of *coke*.

767. The benzene radicals, $(C_6H_5)'$, $(C_6H_4)''$, $(C_6H_3)'''$, etc., by their union with other radicals, form series of hydrocarbons, chlorides, alcohols, aldehydes, acids, amines, etc., which resemble those of the paraffins, besides a few which are unique. Among the latter are the *phenols*, so named from the first member, C_6H_5OH, commonly known as carbolic acid; the *quinones* are a sort of peroxides, as $(C_6H_4)''O_2$, containing the diatomic radical O_2; and there are also "diazo" compounds, containing the double nitrogen group, $=N\cdot N=$ or $-N:N-$.

768. Some benzene hydrocarbons, C_nH_{2n-6}.

Containing: $(C_6H_5)'$.	Containing: $(C_6H_4)''(C_6H_3)'''(C_6H_2)^{iv}$, etc. Each with 3 isomers (o. m. p.), etc.
C_6H_6, benzene. C_7H_8, toluene, or methyl benzene.	
C_8H_{10}, ethyl benzene.	$C_6H_4(CH_3)_2$, xylene.
C_9H_{12}, propyl benzene, cumene (isopropyl).	Ethyl methyl benzene, pseudo-cumene, and mesitylene, $C_6H_3(CH_3)_3$.
$C_{10}H_{14}$, isobutyl benzene.	$C_6H_4\cdot CH_3$, C_3H_7, cymene, etc., ethyl dimethyl benzene, durene, $C_6H_2(CH_3)_4$.
$C_{11}H_{16}$, isoamyl benzene.	Laurene, methyl diethyl benzene, $C_6H(CH_3)_5$, and many others.
$C_{12}H_{18}$, isohexyl benzene.	Hexa methyl benzene, $C(CH_3)_6$.

Yield, on complete oxidation,

Benzoic acid,	Ortho, meta, and para acids.

769. Benzene, C_6H_6, is manufactured on the large scale by redistilling the light oil of tar, and collecting apart the portion which boils below 90°. This is agitated with strong H_2SO_4, washed with water and again distilled. This distillate is cooled to —12°, when the benzene crystallizes out, and is freed from the adhering liquid homologues by pressure. It may also be obtained pure by distilling benzoic acid, or its salts, with quicklime, $C_6H_5COOH + CaO = CaOCO_2 + C_6H_6$.

Pure benzene is, at ordinary temperatures, a bright, colorless liquid, of peculiar ethereal odor; sp. gr., 0.9; boils, 80.5°. It is readily volatilized, and burns in the air with a luminous, but smoky flame. It solidifies at 0° to a mass of fern-like crystals, which melt again at about 5°C.

It is used as a solvent for the fats, resins, caoutchouc, and also dissolves phosphorus and sulphur. Its principal use in the arts is as the starting-point in the manufacture of the aniline colors.

Di-phenyl, $C_6H_5 \cdot C_6H_5$, is formed when benzene vapor is passed through red-hot tubes.

770. The hydrocarbons homologous with benzene, increase by CH_2, and are formed by substituting methyl, or some other monovalent alkyl radical, in place of hydrogen atoms. Those that contain the univalent radical phenyl, C_6H_5, as toluene, ethyl benzene, and cumene, are the true homologues of benzene, and resemble it closely, but have higher boiling and solidifying points. All these are oxidized by chromic mixture to benzoic acid, C_6H_5COOH, plus other products dependent on the constitution of the alkyl radical. *Toluene* is one of the products of the distillation of tolu balsam. *Cumene* and

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NOTE.—Benzene is sometimes called benzol and benzine; the termination "ol" is reserved for the alcohols; the lighter paraffins are also called benzene.

cymene, occur in certain fragrant oils, as cumin and caraway. All of these may be formed synthetically by the action of sodium upon a mixture of two mono-haloids, which contain the required benzene and alkyl radicals; as, $Na_2 + C_6H_5Br + C_2H_5I = NaI + NaBr + C_6H_5C_2H_5 =$ *ethyl benzene.*

The several metameric series which contain $(C_6H_4)''$, $(C_6H_3)'''$, and $(C_6H_2)^{iv}$, may be produced by analogous reactions, but often more conveniently by decomposing their respective acids with quicklime. Each of these should have, by theory, its three isomers,—ortho, para, and meta, etc.,—and each of the latter its own system of derivatives. Among these are to be noted:

I. The *xylenes*, $C_4H_4(CH_3)_2$, so-called because they are also found in wood-tar. They yield, by partial oxidation, *ortho-toluic*, *meta-toluic*, and *para-toluic* acids, $CH_3 \cdot C_6H_4 \cdot COOH$ (metamers of *alpha-toluic* acid, $C_6H_5 \cdot CH_2 \cdot COOH$); and (2), by complete oxidation the bi-basic acids, $C_6H_4(COOH)_2$; viz, *phthalic* (*ortho*), *iso-phthalic* (*meta*), and *tere-phthalic* (*para*). Phthalic acid is usually obtained by oxidizing naphthalene.

II. The trimethyl benzenes, $C_6H_3(CH_3)_3$, are all found in the coal-tar oils which boil between 160° and 170°; viz, mesitylene (1, 3, 5), pseudo-cumene (1, 3, 4), and the consecutive modification (1, 2, 3), not yet obtained pure. Mesitylene is also obtained from acetone, $3(CH_3 \cdot CO \cdot CH_3) - 3H_2O = C_9H_{12}$. When oxidized by dilute nitric acid, it yields (1) mesitylenic acid $(CH_3)_2C_6H_3COOH$; (2) mesidic or uvitic acid, $CH_3 \cdot C_6H_3 \cdot (COOH)_2$; and (3), trimesic acid, $C_6H_3(COOH)_3$.

III. Fourteen hydrocarbons, $C_{10}H_{14}$, are already known. Special interest attaches to *cymene*, because it may be formed from the terpenes, $C_{10}H_{16}$, such as oil of orange, and because it may be obtained by heating camphor with P_2S_5, and also from cumic acid, $C_3H_7 \cdot C_6H_4 \cdot COOH$. It boils at 175°; sp. gr., 0.87; oxidizes to para-toluic and to tere-phthalic acids, and is, therefore, para methyl propyl benzene, $C_3H_7 \cdot C_6H_4 \cdot CH_3$.

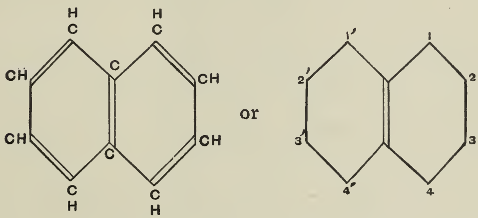
771. Other hydrocarbons. Twenty-two different series of hydrocarbons have been partially investigated, reaching from C_nH_{2n+2} to C_nH_{2n-40}. Those remaining to be described, and whose constitution is known, may be referred to complex nuclei, which contain (1) benzene

radicals united to those of the olefines, etc.; (2) benzene radicals united together; or (3), mixtures of these two types. Most of these have been formed synthetically; a great number—balsams, resins, etc.—have been found in the exudations of trees, and among the products of destructive distillation.

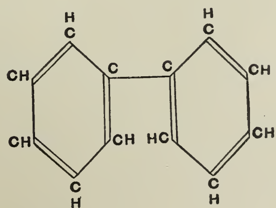
772. The important member of the series, C_nH_{2n-8}, is styrolene or cinnamene, $C_6H_5 \cdot CH : CH_2$, which is *ethenyl-benzene.* It may be obtained by distilling storax with water, or cinnamic acid with lime. It is a thin, oily liquid, of aromatic odor (sp. gr., 0.924; boils at 145°), which changes on keeping to a solid polymer, called meta-styrolene.

Acetenyl benzene, $C_6H_5 \cdot C \vdots CH$, the only known member of the series, C_nH_{2n-10}, resembles acetylene.

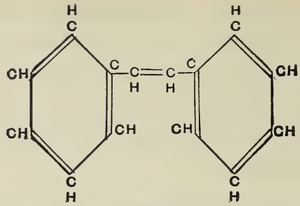
The *remaining hydrocarbons* contain two or more benzene groups; as,



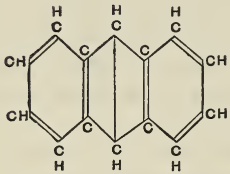
C_nH_{2n-12}, as, Naphthalene; $C_{10}H_8$, or $C_6H_4 \cdot C_4H_4$.



C_nH_{2n-14}; as, Di-phenyl, $C_{12}H_{10}$, or $C_6H_5 \cdot C_6H_5$.



C_nH_{2n-16}; as, Stilbene, $C_{14}H_{12}$.



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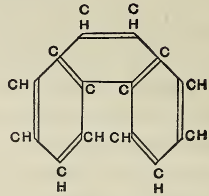
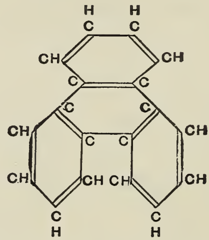


C_nH_{2n-18}, as, Anthracene, $C_{14}H_{10}$, and Phenanthrene.



C_nH_{2n-24}; as, Chrysene, $C_{18}H_{12}$.

773. Naphthalene, $C_{10}H_8$, is produced when the vapors of most other hydrocarbons are strongly heated. Accordingly, it is a bye product in the manufacture of coal-gas, and may be obtained in large quantities from the coal-tar which distils between 150° and 220°. It forms in white rhombic plates, of faint odor and burning taste, which melt at 79°C, and boil at 218°; sp. gr., 1.14. It is soluble in alcohol and ether.

It resembles benzene in its chemical properties, but has a much greater number of isomeric substitution prod-

ucts. It unites directly with chlorine, forming first additive products, like $C_{10}H_8Cl_2$, and $C_{10}H_8Cl_4$. Also, after distilling these chlorides with KHO, substitution products, as monochlor naphthalene, $C_{10}H_7Cl$, which has two isomers; di-chlor naphthalene, $C_{10}H_6Cl_2$, which has ten isomers, etc., etc., to perchlor napthalene, $C_{10}Cl_8$.

Nitric acid produces similar substitution products, as $C_{10}H_7NO_2$, and also oxidizes it to ortho-phthalic and oxalic acids, $C_{10}H_8 + O_2 = (COOH)_2 + (C_6H_4)(COOH)_2 =$ phthalic acid. (Page 444.)

774. Anthracene and phenanthrene, $C_{14}H_{10}$, are obtained on the large scale from that portion of coal-tar which distils between 340° and 400°. They resemble each other in forming colorless tablets with a fine, blue fluorescence. Phenanthrene has a lower melting point (100°), and is separated from its isomer by its greater solubility in boiling alcohol. Anthracene melts at 213° and is somewhat soluble in warm benzene.

Anthracene has recently attained commercial importance as the source from which *alizarin*, the coloring principle of the madder-root, may be artificially produced (1) by oxidizing the anthracene to anthraquinone, $C_6H_4(CO)_2C_6H_4$; (2) this becomes anthraquinone di-sulphonic acid when treated with strong sulphuric acid, $C_{14}H_6O_2(SO_2OH)_2$. (3) The product fused with potash changes to potassium alizarine, $C_{14}H_6O_2(OK)_2$. (4) The fused mass is dissolved in water, from which HCl precipitates alizarine, which is di-hydroxy-anthraquinone, $C_6H_4(CO)_2C_6H_2(OH)_2$.

Alizarine crystallizes in yellowish-red prisms, which may be sublimed at 290° into long red needles. It may be reduced to anthracene by heating with zinc dust, or be oxidized by nitrous acid to anthraquinone and to phthalic acid. It is a weak bibasic acid, soluble in alkalies, with a violet color.

From this solution the "madder lakes" of the dyer are prepared (with lime salts, a blue; with iron, violet; with alum, a fine red). The famous "Turkey red" is due to an alum lake treated with oil.

Alizarine was formerly produced by fermenting the madder-root, which contains a glucoside, ruberythic acid, $C_{26}H_{28}O_{14} = (C_{14}H_8O_4 + 2C_6H_{12}O_6 - 2H_{2}O)$. Old madder-root contains also

purpurine, $C_{14}H_5O_2(OH)_3$. Madder-root, when boiled with dilute sulphuric acid, yields a mixture of alizarine and purpurine, which is known as *garancine.*

775. Pyrene, $C_{16}H_{10}$, and **chrysene,** $C_{18}H_{12}$, are the last distillation products of coal-tar. Among other bodies of this group are *retene,* $C_{18}H_{18}$, found fossil and in pine-tar, and the fossil resins *ozocerite*, *fichtelite*, and *asphaltum.*

Terpenes and Resins.

776. Among the natural secretions of many tropical plants and of the coniferous trees, are a number of odorous substances which are known in commerce as essential oils, turpentines, balsams, and resins. Most of them are mixtures which contain bodies belonging to different chemical groups. Some of the "essential oils" contain acids, as pelargonic acid; many are ethers, as the oil of wintergreen; some aldehydes, as the oil of bitter almonds; some phenols, as thymol; and some are sulphur-oils, as the mustard-oils; but a very large number consist chiefly of hydrocarbons polymeric with C_5H_8. These are roughly grouped by differences in their boiling points.

777. Those that distil between 160°–170° are called the terpenes, $C_{10}H_{16}$. An unusual number of isomers (32) having this empirical formula are known. They agree in almost all of their properties,—chemical and physical,—but differ in odor, and sometimes also in their relations to polarized light. Among these are the volatile oils of orange, neroli, lemon, lime, and bergamotte, from the genus citrus; the volatile oils of beech, caraway, camomile, coriander, elemi, juniper, laurel, parsley, pepper, savin, and thyme. The oils of rose and cubebs, and that in balsam of copavia, are polymers of C_5H_8.

778. These volatile or essential oils are obtained from flowers, fruits, and other parts of plants by pressure or by distillation with water.

They have a pungent odor and taste, and produce upon paper a greasy stain, which soon disappears. In their chemical actions, they behave like turpentine. The crude turpentines are semi-fluid balsams, which exude from incisions made in the bark of various species of pines, larches, and firs. The principal varieties are the North Carolina, the Bordeaux, the Venice turpentines, and Canada balsam. When these are distilled, either alone or with water, they yield the volatile oil of turpentine, and leave behind a solid resin, colophony. The oils of turpentine are mixtures of several isomers of *terebenthine*, $C_{10}H_{16}$, which turns the plane of polarization to the left, and of *australene*, $C_{10}H_{16}$, which is dextro-rotatory.

The purified oils of turpentine are thin colorless liquids, of a somewhat disagreeable odor; specific gravity, 0.87; boil at 161°. They are nearly insoluble in water, but are freely miscible with alcohol and ether. They are solvents of the fixed oils and the resins, and are largely used in making paints and varnishes.

When exposed to the air, turpentine rapidly absorbs oxygen, which it again yields in the form of hydrogen peroxide on being warmed with water. Chlorine, bromine, and iodine act energetically upon it. In most cases two isomeric compounds are produced, one solid and the other liquid. The solid hydrochloride, $C_{10}H_{16}HCl$, has the odor of camphor. Strong nitric acid decomposes it with great violence.

779. The camphors are very nearly related to the terpenes, and appear to be the solid products of their oxidation. Common or laurel camphor, $C_{10}H_{16}O$, is obtained from the camphor-tree of Japan. This or its isomer has been produced artificially from cymene. It is a tough, translucent mass, a very little lighter than water (0.98), of peculiar taste and odor. It sublimes at ordinary temperatures, fuses at 175°, and distils at 204°.

It is largely used as a destroyer of moths, and as a household medicine. It is but slightly soluble in water, but readily in alcohol and the essential oils. When heated in alcoholic solution with caustic potash, it is decomposed into borneol and camphic acid, $C_{10}H_{15}O \cdot OH$.

Borneol, or Borneo camphor, $C_{10}H_{17}OH$, strongly resembles laurel camphor, but has a more peppery taste and odor. It may be converted into laurel camphor by nitric acid. Both these camphors yield, by abstraction of water, *cymene*, $C_{10}H_{14}$, and other hydrocarbons.

Menthol, $C_{10}H_{20}O$, occurs in the oil of peppermint, and yields, by abstraction of H_2O, menthene, $C_{10}H_{18}$.

780. The balsams are mixtures of the volatile oils and the resins. When first obtained, they are generally thick liquids, but gradually harden on exposure to the air. Besides the crude turpentines already mentioned, are others, which contain, in addition, benzoic and cinnamic acids, as Peru and tolu balsams, storax and gum benzoin.

The resins are brittle amorphous bodies, which are insoluble in water, but are soluble in alcohol and in the volatile oils. Common resin, or colophony, is a good example. Most of them are mixtures, containing various acids; colophony containing two isomers, sylvic and pimaric acids, $C_{20}H_{30}O_2$.

Copal, sandarac, dragon's blood, mastic, and lac are used extensively in varnishes. The lac results from the sting of an insect upon certain East Indian trees. While in its crude state, it is called stick-lac, or seed-lac, and contains a red dye, which is due to the insects. When purified, it forms the well known shellac, the chief ingredient of good sealing-wax. Amber is a fossil resin, yielding, on distillation, amber oil, succinic acid, and two resins.

781. The gum resins are mixtures of hard resins, oils, and gums. Among these are aloes, asafœtida, galbanum, guaiacum, myrrh, etc. Burgundy pitch and Mecca balsam are *oleo-resins*.

Caoutchouc, or India rubber, is found in the juices of many plants growing in the tropics. It is a mixture of several isomeric terpenes. When pure, it is a soft, white mass, characterized by great elasticity. It is soluble in naphtha and carbon bisulphide, and is left unchanged when these solvents evaporate. It combines with sulphur to form what is known as vulcanized rubber.

The ordinary vulcanized rubber is produced by heating caoutchouc with a small quantity of sulphur (5–10%) to about 140°. The vulcanized rubber differs in many respects from the natural caoutchouc, being less readily soluble, and better able to resist the action of the atmosphere and of chemical re-agents. It is used extensively in rubber tubing, over-shoes, etc. *Ebonite* is the hard rubber used in knife handles, buttons, etc., and contains a larger amount of sulphur, carefully incorporated by heating and pressure.

Gutta-percha is the thickened juice of the *Isonandra gutta.* It is a tough, inelastic substance, similar in many respects to caoutchouc. When heated in boiling water, it softens, and becomes so pliable that it can be made to assume any form, and retains this on cooling. It is extensively used for insulating telegraph wires.

Recapitulation.

(1) The aromatic hydrocarbons are regarded as formed upon the benzene nucleus, C_6H_6.

(2) Two benzene groups may unite, as in di-phenyl, $C_6H_5 \cdot C_6H_5$, and so uniting suffer condensation.

(3) The benzene nucleus, whether simple or condensed, may be modified by changes within the nucleus, or by additions of "lateral chains," and so give rise to two classes of isomers.

(4) The di-derivatives form ortho, meta, and para compounds,— o, m, p. The tri-derivatives form consecutive, 1, 2, 3; symmetrical, 1, 3, 5; and unsymmetrical compounds, 1, 2, 4.

(5) Many of these are obtainable from coal-tar, as benzene, anthracene. The terpenes are natural hydrocarbons, related to cymene. Many essential oils are isomers of terpene.

The camphors are oxidized terpenes.

(6) Many of the hydrocarbons are useful in the arts, as turpentine, the resins, and balsams. The others are important by reason of their derivatives, notably the "coal-tar colors."

Partial Summary of the Oils.

- **I. Fixed Oils and the Fats.**
  - Glycerides.
    - Unctuous; as,
      - Tallow.
      - Palm-oil.
      - Lard-oil.
      - Olive-oil.
      - Walnut-oil.
    - Castor-oil.
    - Drying; as,
      - Poppy.
      - Hemp.
      - Linseed.
  - Ethereal salts; as, the waxes and spermaceti.
- **II. Volatile, or Essential, Oils.**
  - Ethereal salts; as, wintergreen.
  - Allyl sulphur ethers; as, garlic.
  - Aldehydes; as, bitter almonds.
  - Phenols; as, thyme.
  - Oxidized terpenes; as, camphors.
  - Terpenes, $C_{10}H_{16}$; as, orange, rose.
- **III. Mineral Oils.**
  - Hydrocarbons,
    - "open chain;" as, paraffins, olefines.
    - "closed chain;" as, benzenes.

CHAPTER XXVII.

AROMATIC COMPOUNDS CONTAINING O AND OH.

782. The aromatic hydrocarbons form two classes of hydroxyl derivatives, which are metameric with each other. (1) *The phenols*, formed by substituting in C_6H_6 the *benzene nucleus*, OH for H, as *phenol*, C_6H_5OH; *catechol*, $C_6H_4(OH)_2$; and *pyrogallol*, $C_6H_3(OH)_3$. (2) *The aromatic alcohols*, formed by the same substitution in the lateral chain; as, *benzyl alcohol*, $C_6H_5CH_2OH$.

PARTIAL LIST OF PHENOLS.

Monohydric.

C_6H_6O,	Phenol, ...	$C_6H_5 \cdot OH$.
C_7H_8O,	Cresols (o. m. p.), . .	$C_6H_4(CH_3)OH$.
$C_8H_{10}O$,	Xylenols, ...	$C_6H_3(CH_3)_2OH$.
	Ethyl phenols (phlorol),	$C_6H_4(C_2H_5)OH$.
$C_9H_{12}O$,	Messitols, . . .	$C_6H_2(CH_3)_3OH$.
	Propyl phenols, . .	$C_6H_4(C_3H_7)OH$.
$C_{10}H_{14}O$,	Thymols, 1, 3, 4, . .	$C_6H_3(CH_3)(C_3H_7)OH$.
	Carvacrols, 1, 2, 4 and carvols.	

Di-hydric.

$C_6H_6O_2$,	Pyrocatechin, resorcin, hydroquinone,	$C_6H_4(OH)_2$.
$C_7H_8O_2$,	Orcin, homo-pyrocatechin, .	$C_6H_3\ CH_3(OH)_2$.
$C_8H_{10}O_2$,	β, orcin, hydrophlorone, .	$C_6H_2(CH_3)_2(OH)_2$.

Tri-hydric.

$C_6H_6O_3$,	Pyrogallol, phloroglucin, . .	$C_6H_3(OH)_3$.

783. The phenols resemble the tertiary alcohols in most of their chemical properties, but were formerly regarded as acids because they form salts, like C_6H_5ONa, by the action of the basic hydroxides. They may be formed from the benzene hydrocarbons (1) by fusing their sulphonic salts with caustic potash, $C_6H_5SO_2OK$, benzene sulphonate $+ KOH = K_2SO_4 + C_6H_5OH =$ *phenol*, or (2), by the action of nitrous acid upon the amines; as, $C_6H_5NH_2$ = aniline $+ NOOH = N_2 + H_2O + C_6H_5OH$.

The principal source of the lower members is the heavy oil of tar already mentioned. To prepare them (1) the crude oil is shaken up with the aqueous solution of an alkali (soda). In the course of time, an alkaline phenate, etc., forms and dissolves in the water. This solution is drawn off and decomposed by hydrochloric acid. The oily product thus formed is separated by fractional distillation. The portion which distills between 180°–200°C is mostly phenol.

784. Phenol, C_6H_5OH, which gives the generic name to this class of compounds, is usually termed *carbolic acid.* When pure, it crystallizes in colorless prisms, which melt at 40°C (boil at 183°C; sp. gr., 1.08), and dissolve in 15 parts of water. Phenol has a smoky odor, a sharp, burning taste, and is a powerful escharotic. It coagulates albumin, and consequently acts as an energetic poison. It is an excellent disinfectant and antiseptic, and is used also in the manufacture of the aniline colors. Its aqueous solution, dropped upon a pine shaving previously moistened by HCl, produces a permanent blue stain; (2) added to ferric chloride solution, yields a beautiful violet; (3) to bromine water, even when very dilute, a white precipitate of tri-brom phenol, $C_6H_2Br_3OH$.

The phenols, when added to alkaline solutions, form white crystalline salts; as, C_6H_5ONa, sodium phenate. Such salts, when heated with alkyl iodides, yield compounds which resemble the mixed ethers. For example, $C_6H_5ONa + CH_3I = NaI + C_6H_5 \cdot O \cdot CH_3 =$ anisol, a

colorless, fragrant liquid, which may also be obtained from the volatile oil of anise.

785. The phenols and their cogeners easily form substitution products, by exchange of hydrogen in the benzene nucleus for Cl, or NO_2, and the like. Many of these products have strongly acid properties. For example, by the action of nitric acid upon phenol, there are formed (1) three mono-nitro phenols, $C_6H_4NO_2OH$; (2) five di-nitro phenols, $C_6H_3(NO_2)_2OH$; (3) two tri-nitro phenols, $C_6H_2(NO_2)_3OH$; and many others are possible. The most important is

Picric acid, $C_6H_2(NO_2)_3OH$ (1:2:4:6), also called carbazotic acid. It may also be obtained from other organic bodies,—as indigo, silk, wool, etc.,—by the action of strong nitric acid. Picric acid is sparingly soluble in H_2O, but readily in C_2H_5OH, and crystallizes out from hot alcohol in beautiful pale-yellow plates, which melt at 122°, and explode when heated strongly. Its alcoholic solution has an intensely bitter taste, and is used as a substitute for hops in beer, and as an excellent yellow dye for silk and wool.

Potassium picrate, $C_6H_2(NO_2)_3OK$, is a yellow salt, which explodes violently both by heating and by percussion. It is used in fire-works.

786. The substances sold as creasote are mixtures. That obtained from coal-tar is principally phenol; that from beech-tar is mainly cresol, but both contain *guaiacol*, and other such bodies. The odor observed in smoked ham and in Scotch whiskey is due to some sort of creasote. *Creasote* is used, as its name implies, as a *flesh preserver*, and is considered a valuable antiseptic.

The three cresols, $C_6H_4CH_3OH$ (ortho, para, meta), are not easily separated. They may be obtained pure from the sulphonic acids of toluene, $C_6H_4CH_3SO_2OH$.

They are isomeric with benzyl alcohol, $C_6H_5CH_2OH$,

but, nevertheless, resemble their homologue, phenol, in most of their properties and reactions.

Three ten-carbon phenols, $C_{10}H_{13}OH$, are known. Thymol is propyl-meta-cresol, found in the oils of thyme and horse-mint. Carvacrol is propyl-ortho-cresol, found in the oil of origanum, but best obtained from its isomer, carvol, which is an alcohol existing in the oil of caraway.

787. The di-hydric phenols resemble the phenols in most of their chemical reactions, except that they have two hydroxyl radicals for exchange. Ferric chloride produces, in the ortho and meta compounds, characteristic colors (green to violet), but oxidizes the para di-hydric phenols to quinones. They may be obtained by fusing the sulphonic acids, or the haloid derivatives of the phenols with caustic potash,

$$C_6H_4BrOH + KOH = KBr + C_6H_4(OH)_2.$$

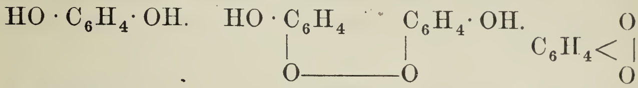
All may be volatilized without decomposition, and most of them may be found among the products of the dry distillation of the aromatic acids, resins, etc., and also of cellulose.

788. Catechol, or pyrocatechin, (o.), $C_6H_4(OH)_2$, is a solid below 104°; boils at 245°, and readily sublimes to shining plates. It is most readily prepared by heating its methyl ether, guaiacol, with hydriodic acid. Guaiacol, $C_6H_3 \cdot O \cdot C_6H_4 \cdot OH$, is a fragrant, colorless liquid, boiling at 200°, obtained from guaiacum resin.

Resorcinol, (m.), $C_6H_4(OH)_2$, is obtained by dry distillation of Brazil wood extract. Its most characteristic reaction is obtained by heating it for a few minutes with phthalic anhydride, $C_6H_4(COOH)_2$, whereby *fluorescein* is produced, which dissolves in dilute alkalies with a splendid green fluorescence.

Hydroquinone, or quinol, (p.), $C_6H_4(OH)_2$, is easiest made by the reduction of quinone with sulphurous acid. Oxidizing agents reconvert hydroquinone to quinone. In

both these operations, an intermediate compound, quinhydrone is produced, which gives a brown color to the solution. Quinone is usually made by oxidizing aniline, $C_6H_5NH_2$, with chromic mixture.

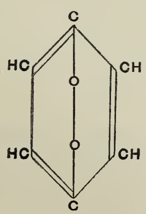


Hydroquinone. Quinhydrone. Quinone.

Hydroquinone crystallizes from an aqueous solution in hexagonal prisms, which have a sweetish taste, and which melt at 169°. *Quinhydrone* crystallizes in splendid gold-green prisms, which form green solutions with alcohol, and brown solutions with hot water.

Quinone, $C_6H_4O_2$, forms golden-yellow needles, more easily soluble in hot water than in cold, which melt at 116°, and volatilize even at ordinary temperatures. The vapor has an odor which resembles that of iodine, and is exceedingly irritating to the eyes.

QUINONE must be taken by the student to represent an entire class of aromatic compounds, produced by the oxidation of the *para* derivatives of the benzene hydrocarbons. In these compounds two hydrogen atoms (1:4) are replaced by two oxygen atoms, united directly to two carbon atoms, either as a dyad group, or after the manner of a double ketone; thus,



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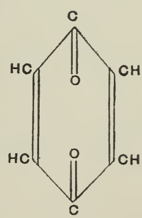


By partial reduction of these bodies quinhydrones are produced; by complete reduction, the para-hydroxy-phenols.

The quinones are usually solids of a yellow color, easily distilled by the aid of steam, and readily forming substitution products with Cl, etc.

789. Orcin, or orcinol, $C_6H_3CH_3(OH)_2$, is found in all those lichens from which archil, cudbear, and litmus are prepared, and results from the decomposition of the acids extracted from them,—orsellinic, erythric, etc. It crystallizes in colorless six-sided prisms, freely soluble in water, and of a sweetish taste.

790. Of the tri-hydric phenols, the most important is *pyrogallol*, or pyrogallic acid, $C_6H_3(OH)_3$. It is prepared by heating gallic acid in a stream of carbonic anhydride, and crystallizes in thin colorless plates, which melt at 115°; sp. gr., 1.45. It has a bitter taste, and is an active poison. When dissolved in the solutions of the alkalies, it rapidly absorbs oxygen from the air, and becomes converted to acetic and carbonic acids and certain brown, humus-like bodies (Exp. 78). It also reduces the salts of gold and silver, and for this reason is sometimes used in photography. Pure ferrous salts give, with pure pyrogallol, only a white cloudiness, but if ferric salts are likewise present, the color becomes first blue and finally red.

Phloroglucol, $C_6H_3(OH)_3$, may be prepared by fusing potassium hydroxide with gamboge, dragon's blood, and similar substances, and from glucosides, like the phloridzin which is found in the root-bark of many fruit-trees. When chlorine is passed into its aqueous solution, phloroglucol is converted to di-chlor acetic acid, $C_6H_6O_3 + 3H_2O + Cl_{12} = 6HCl + 3(C_2Cl_2H_2O_2)$.

791. Besides the phenol dyes occuring naturally, like litmus, may be mentioned a few artificially prepared.

Aurine, or *coralline*, is a fine scarlet-red dye, produced by heating a mixture of phenol and sulphuric acid, and then gradually adding oxalic acid until CO_2 ceases to be evolved; as,

$3(C_6H_5OH)+(COOH)_2=CH_2O_2$, formic acid$+C_{19}H_{14}O_3=$aurine.

The reaction is in reality more complex, and the product a mixture, from which pure aurine, $C_{19}H_{14}O_3$, may be obtained as ruby-red crystals of a fine green lustre.

Rosolic acid, $C_{20}H_{16}O_3$, is the homologue of the preceding, and is made from rosaniline by the action of nitrous acid. It closely resembles aurine in appearance and properties. When heated above 270° it yields phenol, and hence may be regarded as intermediate between the hypothetical *phthaleïn* and *rosaniline* (§ 824).

$$\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\!\!>C<\!\!\begin{array}{l} C_6H_5 \\ H \end{array} \qquad \begin{array}{l} OHC_6H_4 \\ OHC_6H_4 \end{array}\!\!>C<\!\!\begin{array}{l} C_6H_3CH_3 \\ | \\ O \end{array}$$

Phthaleïn. Rosolic acid.

$$\begin{array}{l} NH_2 \cdot C_6H_4 \\ NH_2 \cdot C_6H_4 \end{array}\!\!>C<\!\!\begin{array}{l} C_6H_3CH_3. \\ | \\ NH_2. \end{array}$$

Rosaniline.

The phthaleïns are prepared by heating the mixture of a phenol and phthalic anhydride, $C_6H_4 : C_2O_3$, with strong sulphuric acid. The phthaleïns are soluble in alkaline liquids with fine and characteristic colors. Such solutions, when boiled with zinc, add H_2, and are reduced to *phthalins*, which are colorless bodies, easily reconverted to the phthaleïns by oxidation, and which dissolve in strong H_2SO_4, losing H_2O, and becoming *phthalidins*. Among these products are:

Phenol phthaleïn, $C_6H_4(CO \cdot C_6H_4 \cdot OH)_2$, a yellowish white powder, soluble in dilute alkalies, with fine red color. This color disappears when the acid is neutralized. It is sometimes employed as an indicator in volumetric analysis.

Fluoresceïn is *resorcin phthaleïn*, $C_6H_4(CO \cdot C_6H_3 \cdot OH)_2O$, which is precipitated from its solutions in alkalies by H_2SO_4 in yellowish flocks, which become of a yellowish-red when dried. The solution in dilute alkalies exhibits a splendid green fluorescence. It is converted by bromine to *eosin*, $C_6H_4(CO \cdot C_6HBr_2 \cdot OH)_2O$, which is sold as a brick-red powder, dissolving in alcohol to a reddish-yellow solution. The trace of an alkali produces in this a splendid golden-green fluorescence. The potassium salt, $C_6H_4(CO \cdot C_6HBr_2 \cdot OK)_2O$, is used for dyeing silk a rose-red color.

792. The aromatic alcohols are mostly primary, containing the group CH_2OH attached to the benzene nucleus in a lateral chain. The most of them are pre-

pared from the corresponding chlorides of the hydrocarbons, or from the natural resins and volatile oils. They agree in most of their chemical properties with the alcohols of the fatty series (1) as to the methods by which they are obtained; (2) as to the products which they may be made to yield, the reactions being in both due to changes which take place in the radicals, CH_2OH and CHOH.

793. Benzyl alcohol, $C_6H_5 \cdot CH_2OH$, occurs in Peru and tolu balsams, principally as benzyl benzoate and cinnamate. It may be prepared from either of these by saponification,

$$C_6H_5CH_2 \cdot O \cdot C_6H_5CO = \textit{benzyl benzoate} + KOH =$$
$$C_6H_5COOK = \textit{potassium benzoate} + C_6H_5 \cdot CH_2OH.$$

Also, by the reduction of its aldehyde, the oil of bitter almonds, or of benzoic acid. It is a colorless liquid, having a faint aromatic odor; sp. gr., 1.063; boiling at 206.5°; insoluble in water, but freely soluble in ethyl alcohol. Weak oxidizing agents convert it into benzoic aldehyde, and stronger into benzoic acid.

Benzyl alcohol is converted by the action of strong HCl into *benzyl chloride*, $C_6H_5CH_2Cl$, a colorless liquid, with pungent vapor, which boils at 176°. This compound is also formed when chlorine is passed into boiling toluene, $C_6H_5CH_3 + Cl_2 = HCl + C_6H_5CH_2Cl$. Benzyl chloride is used in the preparation of most benzyl compounds. (1) Giving, with KHS, benzyl mercaptan, $C_6H_5CH_2SH$, and other sulphides; (2) with NH_3, benzyl amine, $C_6H_5CH_2NH_2$, a substance from which the mustard-oils, etc., have been prepared; (3) when boiled with the potassium salts of the organic acids, forming the ethereal salts of benzyl; as, benzyl acetate,

$$C_6H_5CH_2Cl + KC_2H_3O_2 = KCl + C_6H_5CH_2 \cdot O \cdot C_2H_3O.$$

794. About a dozen higher homologues have been described. Among them are the secondary *phenyl-ethyl al-*

cohol, $C_6H_5 \cdot CHOH \cdot CH_3$, which oxidizes to the ketone, $C_6H_5 \cdot CO \cdot CH_3$, *aceto-phenone*, and *benzhydrol*,

$$C_6H_5 \cdot CHOH \cdot C_6H_5,$$

which oxidizes to *benzophenone*, $C_6H_5 \cdot CO \cdot C_6H_5$, and *triphenyl carbinol*, $(C_6H_5)_3COH$.

795. Cumyl alcohol, $C_{10}H_{14}O$, which, together with *cymene*, occurs in Roman caraway oil, bears the same relation to the ten carbon phenols and cymene that benzyl alcohol does to the cresols and toluene.

Cinnyl alcohol, $C_6H_5 \cdot CH : CH \cdot CH_2OH$, is supposed to contain the monovalent allyl, $(CH_2 : CH \cdot CH_2)'$. It may be obtained by distilling a mixture of storax with caustic potash, in silky needles, which have the pleasant odor of hyacinths, and which melt at 33°C to an oily liquid. Upon oxidation, it is converted to cinnamic aldehyde, and then to cinnamic acid. It is, therefore, related to these substances in the same way that allyl alcohol is related to acroleïn and to acrylic acid.

796. Cholesterin, $C_{25}H_{41}CH_2OH$, occurs in various parts of the animal system, but especially in the brain and the bile. The biliary calculi are frequently almost pure cholesterin. It may be obtained by dissolving these in a mixture of alcohol and ether. Upon crystallizing, it forms in white plates of a fatty feel, and a mother-of-pearl lustre, melting at 145°; sp. gr., 1.06. It is soluble in chloroform. The chloroform solution, shaken with an equal volume of strong sulphuric acid, becomes at first blood-red, and finally purple, while the acid takes on a greenish fluorescence. If the chloroform solution be then decanted and allowed to evaporate, it becomes blue, then green, and at last yellow. These reactions serve as a test for cholesterin.

797. The phenol alcohols contain two or more hydroxyl groups, one of which is directly united to the

nucleus, and one in the lateral chain. They are prepared by reducing their aldehydes with sodium amalgam.

Saligenin, $HO \cdot C_6H_4 \cdot CH_2OH$, is ortho-oxybenzyl alcohol, best made from *salicin* (a glucoside found in willow bark) by the action of the ferment, *emulsin*; thus, $C_{13}H_{18}O_7$, salicin $+ H_2O = C_6H_{12}O_6 + C_7H_8O_2$, saligenin. After the mixture has been digested for a day, the alcohol is extracted by shaking with ether, and purified by recrystallizing. It forms rhombic tables which melt at 82°, and sublime below 100°; sp. gr., 1.16. It is soluble in water, and is easily converted by oxidizing agents into salicylic aldehyde and salicylic acid.

798. Very interesting are a number of substances of this group, which contain methyl oxide in place of the phenol hydroxyl, in the same sense of the words that anisyl alcohol, $CH_3O \cdot C_6H_4 \cdot CH_2OH$, may be regarded as the methyl ether of saligenin, and which may easily be prepared by boiling anisic aldehyde with an alcoholic solution of potash.

Vanillic alcohol, $CH_3O, OH, C_6H_3 \cdot CH_2OH$, is obtained by the oxidation of the vanillin in vanilla beans, and also from coniferin. *Coniferin*, $C_{16}H_{22}O_8$, is a crystalline glucoside found in the cambium larger of pine trees. It forms, on fermentation,

coniferyl alcohol, $CH_3O, OH, C_6H_3 \cdot CH : CH \cdot CH_2OH$.

Eugenol, $CH_3O, OH, C_6H_3 \cdot CH : CH \cdot CH_3$, occurs in the oils of cloves and of pimento. The two latter contain the radical allyl, and are closely related to *ferulic acid*, $(OH)_2 : C_6H_3 \cdot C_3H_4COOH$, which is found in asafœdita. All of these compounds may be made to yield protocatechuic acid, $C_6H_3(OH)_2COOH$.

A few phenols have been described which contain two or three benzene nuclei. Among these are *di-phenol*, $HO \cdot C_6H_4 \cdot C_6H_4 \cdot OH$; α and β *naphthols*, $C_{10}H_7OH$;

and the metamers, *anthranol* and *anthrol*, $C_{14}H_9OH$. Also, oxidation products, like—

$$\textit{naphthoquinone},\ C_{10}H_6{<}{\genfrac{}{}{0pt}{}{O}{O}}{>},$$

which, on further oxidation, is converted to (ortho) phthalic acid, $C_6H_4(COOH)_2$, and the very important

$$\textit{anthraquinone},\ C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6H_4.\ \S\,774.$$

The Aldehydes.

799. The aldehydes of these alcohols are constituents of many of the oils found in the spices and flavors.

Benzaldehyde is the oil of bitter almonds, $C_6H_5 \cdot CHO$. It is prepared from *amygdalin* by the fermentation induced by emulsin. These substances are found in the milk of almonds and similar stone-fruits, and the decomposition takes place when the crushed almonds are digested for for some hours with luke-warm water, $C_{20}H_{27}NO_{11}$,

$$\text{amygdalin} + 2H_2O = 2C_6H_{12}O_6 + HCN + C_6H_5 \cdot CHO.$$

Glucose and prussic acid are produced at the same time. It is freed from these by shaking the crude product with Fe_2Cl_6 and $Ca(OH)_2$, and distilling. It may also be prepared from numerous other substances; as, toluol, $C_6H_5CH_3$, benzoic acid, and the albumins.

Pure benzaldehyde is a colorless liquid, of a peculiar aromatic odor, and is not poisonous; sp. gr., 1.063; boils at 179°. It is readily soluble in alcohol, very sparingly in water, and is used for flavoring confectionery. It oxidizes, when exposed to the air, to benzoic acid; is reduced by sodium amalgam to benzyl alcohol.

All the aromatic aldehydes, like those of the fatty series, form beautiful crystalline compounds with the alkaline bi-sulphites, but they behave differently with ammonia, forming neutral bodies known as *hydramides*. Hydro-benzamide is formed by the reaction, $3C_6H_5 \cdot CHO + 2NH_3 = 3H_2O + (C_6H_5CH)_3N_2$. When heated to

130° it becomes the strongly basic *amarine*, $C_{21}H_{18}N_2$, which is its isomer. The latter is poisonous; the former is not. Both are readily soluble in alcohol.

800. Cumic aldehyde, $C_6H_4 \cdot C_3H_7$, CHO, is found in the oils of cumin and water hemlock, together with cymene. It may be obtained from these by first forming its compound with acid sodium sulphite, and then distilling this product with caustic soda. It is a liquid having the odor of caraway seeds; sp. gr., 0.98; boils at 237°; and is converted by alcoholic potash to cumyl alcohol and potassium cumate.

801. Cinnamic aldehyde, $C_6H_5 \cdot CH:CH \cdot CHO$, is the chief constituent of the oils of cinnamon and cassia. It may be made synthetically by saturating a mixture of benzaldehyde and acetic aldehyde with HCl, and heating $C_6H_5CHO + CH_3CHO = H_2O + C_6H_5 \cdot CH:CH \cdot CHO$ (see § 668). It is a colorless liquid, heavier than water, and oxidizing, on exposure to the air, to cinnamic acid, and then to benzaldehyde.

802. Salicylic aldehyde (o.), $OH \cdot C_6H_4 \cdot CHO$, occurs in the flowers of the spiræas. It may be prepared from saligenin by oxidizing with chromic mixture, or more easily by heating a mixture of chloroform, sodium hydroxide, and phenol:

(*a*) $CHCl_3 + 3NaHO = H_2O + HCOOH =$ formic acid.

(*b*) $HCOOH + C_6H_5OH =$

$$H_2O + HO \cdot C_6H_4 \cdot CHO = \text{salicylic aldehyde.}$$

At the same time its isomer, *para oxybenzoic aldehyde*, is formed; the two are separated by distillation, the salicylic aldehyde passing over as an aromatic oil, slightly soluble in water, and boiling at 196°; sp. gr., 1.17. As it contains the phenol hydroxyl, it has weak acid properties, and is sometimes, but improperly, termed salicylous acid.

The oils of anise, fennel, etc., contain *anethol,* $CH_3O \cdot C_6H_4 \cdot C_3H_5$, which is probably the methyl ether of allyl phenol. On warming these oils with dilute nitric acid, anisic aldehyde is produced, $CH_3O \cdot C_6H_4 \cdot CHO$. This is a fragrant liquid; sp. gr., 1.12; boiling at 250°; and is readily converted to anisyl alcohol, and to anisic acid.

About two per cent of *vanillin,* $CH_3O \cdot C_6H_3 \cdot OH, CHO$, is found in vanilla beans, often in crystals. It may be obtained artificially from coniferin by oxidation with chromic acid mixture. It is the methyl ether of the aldehyde of protocatechuic acid. Vanillin crystallizes in groups of colorless needles, which melt at 80°, and sublime at 150°. The well known vanilla flavoring extract is made from it.

The Aromatic Acids.

803. Many of the aromatic acids occur among the natural products of plants and animals; others are prepared from the aromatic hydrocarbons by oxidation with chromic mixture. So, also, like the acids of the fatty series, they may be obtained by oxidizing their aldehydes and alcohols, and they may be reduced to these compounds by nascent hydrogen. They differ from the fatty acids in some particulars, being all of them solids, having comparatively high melting and boiling points, slightly soluble in water, but easily in alcohol and ether. All of them may be distilled by the aid of steam, and some may be sublimed in the dry state without decomposition. The sodium salts of these acids may be prepared synthetically by the joint action of sodium and carbonic anhydride upon their mono-brom derivatives; as, *e. g.*, sodium benzoate; thus,

$$C_6H_5Br + Na_2 + CO_2 = NaBr + C_6H_5 \cdot COONa,$$

and the acid obtained free by subsequent treatment of the product with strong hydrochloric acid.

The calcium salts of the aromatic acids, (1) heated by themselves, produce ketones; *e. g.*,

$$(C_6H_5 \cdot COO)_2Ca = CaCO_3 + (C_6H_5)_2 : CO = \textit{benzophenone};$$

(2) heated with calcium formate, they produce the corresponding aldehyde; as,

$$(C_6H_5COO)_2Ca + (HCOO)_2Ca = 2CaCO_3 + 2(C_6H_5CHO) = \textit{benzaldehyde},$$

which may be reduced to the primary alcohol; as, *benzyl alcohol*, $C_6H_5CH_2OH$. The acids, heated with quicklime, exchange the COOH group for H, and evolve a hydrocarbon; as, $C_6H_5COOH + CaO = CaCO_3 + C_6H_6 =$ *benzene.*

804. Benzoic acid, C_6H_5COOH, is a constituent of various gums and balsams, and is one of the products of the oxidation of a great variety of organic substances. Its chief source is *hippuric acid,* which is found in the urine of herbivorous animals, and which is decomposed on boiling with acids into glycocine and benzoic acid, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH + H_2O = CH_2 \cdot NH_2, COOH + C_6H_5COOH$. It is best prepared by heating gumbenzoin in an iron pan, loosely covered by a hood of filter paper. The acid begins to sublime at about 100°, and collects upon the paper in shining, feathery crystals, which melt at 121° and boil at 249°. Its vapors, when dilute, have a pleasant aromatic odor, but when freely evolved produce coughing.

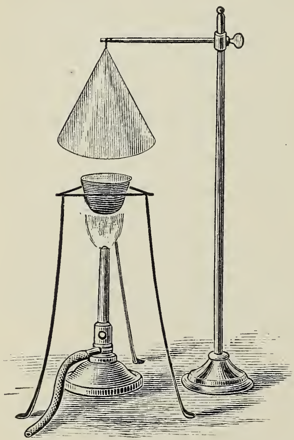


Fig. 108.

The salts of benzoic acid resemble the acetates. The alkaline benzoates are freely soluble in water, and produce, when added to hot neutral solutions of ferric salts, a red-brown amorphous precipitate of basic ferric benzoate, which is quite insoluble in water.

The ethers are of much higher boiling point than those of acetic acid, ethylic benzoate, $C_2H_5 \cdot O \cdot C_7H_5O$, boiling at 211°.

The liquid portion of Peru balsam is chiefly benzylic benzoate, $C_6H_5CH_2 \cdot O \cdot C_6H_5CO$, which boils at 345°.

805. A very large number of derivatives have been obtained from benzoic acid. For example, when it is distilled with PCl_5, it yields C_6H_5COCl, *benzoyl chloride*, a pungent-smelling, colorless liquid, boiling at 199°, and exceedingly active in metathetical reactions, forming (1) with KBr, KCN, etc., benzoyl bromides, cyanides, etc.; (2) with sodium salts of the organic acids, a variety of anhydrides; as, *benzoic anhydride*, $(C_7H_5O)_2O$; *aceto-benzoic anhydride*, $C_2H_3O \cdot O \cdot C_7H_5O$; (3) with ammonia, *benzamide*, $C_6H_5CONH_2$, a weak base soluble in hot water; and, finally, *benzo-nitril*, C_7H_5N; (4) with silver glycocine, *benzoyl glycocine*, which is *hippuric acid*,

$$CH_2 \cdot NAgH \cdot COOH + C_6H_5 \cdot COCl = AgCl + C_7H_5O \cdot NH \cdot CH_2 \cdot COOH,$$

which is found to the extent of about 2% in the urine of oxen and horses, and sometimes in human urine.

It will be observed that all these are changes which take place in the lateral chain,

$$(COOH), (COCl), (CONH_2), (CH_2OH), \text{etc.}$$

806. Other substitutions are known in which a hydrogen atom has been replaced in the *benzene nucleus* by Cl, NO_2, NH_2, etc., in precisely the same manner as in the benzene substitution products. For example, (1) Nitro benzoic acids (o. m. p.), $C_6H_4NO_2 \cdot COOH$, are formed when benzoic acid is treated with a mixture of KNO_3 and H_2SO_4; and (2), these are reduced by nascent hydrogen ($Zn + HCl$) to the *amido-benzoic acids*, (o. m. p.), $C_6H_4 \cdot NH_2$, COOH, which resemble glycocine, but which, when strongly heated, break up into CO_2 and *aniline*, $C_6H_5NH_2$. The ortho-amido-benzoic acid

is known as anthranilic acid, and may be obtained by oxidizing indigo. (3) There are three monochlor benzoic acids, $C_6H_4Cl \cdot COOH$, *chlorbenzoic* (meta), derived directly from benzoic acid by the action of chlorine, *chlorsalicylic* (ortho), from salicylic acid by PCl_5, and *chlordracylic* (para), from para chlortoluene.

All these are *mono* derivatives from C_6H_5COOH, and contain the residue $(C_6H_4COOH)'$. This monovalent radical may be united with OH, with COOH, with CH_3, with C_6H_5, and similar monovalent groups to form a large number of compounds of greater or less importance. There are also *di*-derivatives based upon the residue $(C_6H_3COOH)''$, as di-chlor, di-nitro, nitro-chlor, and nitro-amido benzoic acids, each with its own series of salts and acids, and each is isomeric with two others; and there are numerous other compounds more complex. They illustrate the wonderful flexibility of the benzene nucleus, as well as the persistence of its properties amid so many changes. Among these are those that follow.

807. Three hydroxy-benzoic acids (o. m. p.) are known, $C_6H_4 \cdot OH, COOH$, which are both phenols and acids. Only the *ortho* compound, *salicylic acid*, is of importance. *Salicylic acid* occurs free in spiræas, and as a methyl ether in oil of wintergreen, $HO \cdot C_6H_4 \cdot COOCH_3$.

It has recently been prepared on a large scale (1) by heating phenol and caustic soda to 180° = sodium phenate, C_6H_5ONa; and (2), exposing this product to a stream of carbonic anhydride until no more phenol distils over,

$$2(C_6H_5ONa) + CO_2 = \overbrace{C_6H_5OH} + C_6H_4ONa \cdot COONa;$$

(3) decomposing the residue, which is di-sodium salicylate, with strong HCl,

$$C_6H_4ONa \cdot COONa + 2HCl = 2NaCl + C_6H_4 \cdot OH, COOH;$$

and (4), finally purifying the crude acid by distillation in superheated steam.

Salicylic acid may be obtained in colorless needles and prisms, which melt at 155°; sp. gr., 1.48; and may be

sublimed, but which at higher temperatures partly decompose into CO_2 and C_6H_5OH = phenol. It dissolves readily in alcohol, very sparingly ($\frac{1}{2000}$) in cold water, but more readily ($\frac{1}{13}$) in boiling. Its aqueous solutions give a characteristic violet with ferric salts.

The *free acid* is odorless, and has an astringent taste. It has been strongly recommended as an antiseptic for food preparations, and as a therapeutic agent in acute rheumatism.

Anisic acid, $CH_3O \cdot C_6H_4 \cdot COOH$, the isomer of the oil of wintergreen is methyl-paraoxy benzoic acid, which may be made directly from anise aldehyde, and obtained in fine needles, which melt at 184°, and boil at 280°.

808. Six di-hydroxy benzoic acids, $C_6H_3(OH)_2COOH$, have been described. One of these, *protocatechuic acid* (1:3:4), requires mention, because it so frequently occurs as one of the decomposition products of the resins, balsams, and other aromatic compounds. It is easiest obtained from *tannins*, like catechu, by (1) melting them with KHO; (2) dissolving the fused mass in hot water; and (3), decomposing the potassium salt by H_2SO_4. It crystallizes in needles, which melt at 199°, and decompose at higher temperatures into CO_2 and *catechol.*

809. Gallic acid, $C_6H_2(OH)_3COOH$, is tri-hydroxy benzoic acid. It occurs in the leaves, fruits, and bark of many plants, as tea, sumach, oak. It is easiest prepared (1) by fermenting powdered gall-nuts, which yield *gallotannic acid;* (2) decomposing this product by boiling with water; and (3), recrystallizing. It forms in silky needles (sp. gr., 1.7), which lose at 120° the one molecule of water of crystallization they contain, melt at 222°, and break up into CO_2 and pyrogallol, $C_6H_3(OH)_3$. It is easily oxidized, and, therefore, reduces the salts of the noble metals, and ferric compounds to ferrous, forming in the last instance a bluish-black precipitate, which

dissolves in excess of Fe_2Cl_6 with a greenish color. When heated with strong H_2SO_4, it yields *rufigallic* acid (related to alizarin), which, when mordanted with alum, yields a beautiful red dye.

810. The tannins are substances widely distributed through the vegetable kingdom, and are characterized by giving, with ferric chloride solution, (1) bluish-black precipitates (gall-nuts, tea-leaves), or (2), greenish precipitates (catechu, kino, sumach, oak-bark). The former class are, for the most part, glucosides of gallic acid, and consequently yield, on dry distillation, *pyrogallol.* The latter yield, on dry distillation, pyrocatechin, and, when fused with potash, protocatechuic acid and phloroglucin. The tannins resemble each other strongly, forming yellowish amorphous bodies, easily oxidized, and becoming brown in the presence of the alkalies, coagulating solutions of gelatin, and having a marked astringent taste, especially noticeable in green fruits, persimmons, etc.

The ordinary *tannin* of the apothecary is prepared by macerating powdered gall-nuts for several weeks in a mixture of ether and dilute alcohol. On filtering this through cotton-wool, the filtrate separates in two layers, the upper ethereal layer containing gallic acid and impurities, the lower aqueous portion almost pure tannin. This is *gallotannic acid*, and is probably the first anhydride of gallic acid, $2(C_7H_6O_5) - H_2O = C_{14}H_{10}O_9$. This sort of tannin is not suited for making leather, but is used in medicine and in making inks.

Writing fluids are usually made by digesting a mixture of gallnuts (2 parts), ferrous sulphate (1 part), and gum arabic (1 part), in water (10 parts) for many days, with frequent agitation. *Ferrous gallotannate* forms, which is prevented from settling out by the presence of the gum. Such an ink will appear faint when first used, but rapidly oxidizes to the black ferric gallotannate. The *black inks* contain ferric salts; *copying inks* an addition of sugar. The aniline inks are merely solutions of aniline.

The best tannin for making leather is obtained from oak, birch, and hemlock barks. The hides are soaked for months in vats which contain water and the ground bark, whereby the gelatin of the hide becomes coagulated throughout, and is prevented from putrefying when taken out and worked into leather. The process is a mechanical one, and the result may be attained in other ways, as by a mixture of alum and salt (white leather), or by kneading with oils and albumin (chamois leather).

Caffe-tannic acid, from coffee berries, yields catechol when heated alone; caffeic acid, $C_6H_3(OH)_2$, $CH:CH \cdot COOH$, when boiled with potash lye; and protocatechuic acid, $C_6H_3(OH)_2COOH$, when fused with KHO. It gives a green color with Fe_2Cl_6.

811. Cinnamic acid, $C_6H_5 \cdot CH : CH \cdot COOH$, occurs in Peru, tolu, and storax balsams. On boiling any of these with soda lye, and decomposing the sodium cinnamate thereby formed, by strong HCl, the free acid is obtained in inodorous needles, melting at 133°, and distilling at 300°; sp. gr., 1.19. It yields benzoic acid in most of its reactions, and may also be formed from benzoic aldehyde.

Atropic and *isatropic* acids, which are formed by boiling the poisonous *atropine* with KHO, are isomers of cinnamic acid, and may be made to undergo similar transformations.

812. Coumaric acid, $C_6H_4 \cdot OH$, $CH : CH \cdot COOH$, is made from *coumarin*, which exists in the tonka bean.

It may be made artificially by boiling together sodium, salicylic aldehyde, and acetic anhydride, $C_6H_4 \cdot ONa$, $CHO + (C_2H_3O)_2O = H_2O + C_2H_3O_2Na + C_6H_4$, $(CH:CH \cdot CO)$, $O =$ *coumarin*. Longer boiling with alkalies converts the coumarin into the acid. Both are reduced by sodium amalgam to hydrocumaric acid, $C_6H_4 \cdot OH$, $CH_2 \cdot CH_2 \cdot COOH$, which is usually obtained from sweet clover. All of these are converted by fusion with KHO to salicylic acid, $C_6H_4 \cdot OH$, $COOH$, and are, therefore, ortho compounds.

813. Tyrosine, or hydroxy-phenyl-amido-propionic acid, $C_6H_4 \cdot OH$, $CH_2 \cdot (CHNH_2) \cdot COOH$, sometimes occurs ready formed in old cheese, and in the liver and pan-

creas. It is prepared from albuminoids by long boiling with acids or alkalies, and in the form of silky needles, difficultly soluble in water, almost insoluble in alcohol and ether, but easily soluble in acids and in alkaline liquids (§ 730).

814. The other aromatic hydrocarbons are also represented by numerous series of acids: (1) Those which contain the phenyl radical C_6H_5, as alpha toluic acid, $C_6H_5 \cdot CH_2 \cdot COOH$, are generally made by boiling their chlorides first with potassium cyanide, and then with potash. These acids yield benzoic acid upon oxidation. (2) The other hydrocarbons, $[(C_6H_4)''$, etc.], when treated with dilute nitric acid, oxidize to mono-basic acids, which are similar to benzoic acids, and may be made to undergo similar transformations. For example, the *xylenes*, $C_6H_4(CH_3)_2$, yield o., m., and p. mono-basic toluic acids, $C_6H_4 \cdot CH_3$, $COOH$, isomeric with alpha toluic acid; which (3), may also be converted by oxidation with potassium permanganate into three isomeric dibasic *phthalic* acids, $C_6H_4(COOH)_2$. *Phthalic acid* (o.) is usually made by oxidizing napthaline dichloride with hot dilute nitric acid. The other two, *isophthalic* (m.), and *terephthalic* (p.), are more stable and are made by oxidizing m. and p. xylenes with chromic mixture; but all are so frequently obtained from other di-benzene derivatives that they serve as guides in classifying such compounds into ortho, meta, and para series. The members of such series differ in crystalline form, solubility, specific gravity, melting point, etc. Phthalic acid is readily soluble in water, and crystallizes in shining tables, which melt at 184°, and decompose into water and *phthalic anhydride*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O$.

In like manner, mesitylene, one of the tri-methyl benzenes, $C_6H_3(CH_3)_3$, yields, successively, mesitylenic acid, $C_6H_3(CH_3)_2COOH$, mesidic acid, $C_6H_3CH_3(COOH)_2$,

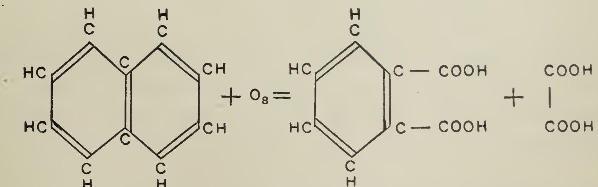
and trimesic acid, $C_6H_3(COOH)_3$; all of them symmetrical (1:3:5). A remarkable series of acids, which are structurally derived from benzene is given below;

$C_6H_5 \cdot COOH$,	Benzoic acid from benzene, $C_6H_5 \cdot H$.		
$C_6H_4 : (COOH)_2$,	Phthalic, 1:2.	Isophthalic, 1:3.	Terephthalic, 1:4.
$C_6H_3 \vdots (COOH)_3$,	Hemimellitic, 1:2:3.	Trimesic, 1:3:5.	Trimellitic, 1:2:4.
$C_6H_2 \vdots (COOH)_4$,	Mellophanic,	Prehnitic, 1:2:3:5.	Pyromellitic, 1:2:4:5.
$C_6H(COOH)_5$,	Wanting.	. . .	. . .
$C_6 \vdots (COOH)_6$,	. . .	. . .	Mellitic.

$H_6 \cdot C_6 \cdot (COOH)_6$, Hydromellitic.

815. Mellitic acid, $C_6 \cdot (COOH)_6$, is found combined with alumina in *honey-stone*, a mineral sometimes found in coal beds. It is reduced by sodium amalgam to *hydromellitic acid*, $C_{12}H_{12}O_{12}$, in which all the double bonds of the benzene chain are unlocked by the entrance of six added hydrogen atoms, $H_6 \cdot C_6 \cdot (COOH)_6$. These two acids are sources from which all of the tetra and tri carboxylic acids of the above table are obtainable.

The foregoing are only a small part of the oxygen compounds known which contain the simple benzene nucleus. Similar compounds are also formed from the conjugated hydrocarbons. For example, *naphthalene*, $C_{10}H_8$, when oxidized, splits up its double ring, and yields phthalic and oxalic acids; thus,



Naphthaline. Phthalic acid. Oxalic acid.

These also yield a great variety of substitution products from which may be formed phenols, quinones, alcohols, acids, etc.

Naphthalene, when treated with strong H_2SO_4, yields two naphthalene sulphonic acids, $C_{10}H_7SO_2OH$, and two naphthalene disulphonic acids, $C_{10}H_6(SO_2OH)_2$. These are sources for further substitution products. Each of the first, when fused with caustic soda, yields a naphthol, $C_{10}H_7OH$; with sodium formate, a naphthoic acid, $C_{10}H_7 \cdot COOH$, for which an aldehyde, $C_{10}H_7 \cdot CHO$, is known, but no alcohol, $C_{10}H_7 \cdot CH_2OH$; with sodium and carbonic acid, an oxy-naphthoic acid, $C_{10}H_6 \cdot OH \cdot COOH$. The disulphonic acids yield, with potassium cyanide, di-cyanides, two naphthalene carboxylic acids, $C_{10}H_6(COOH)_2$, and the like. These compounds, as well as those derived from anthracene, chrysene, etc., will be sufficiently mentioned when treating of their products, as the mode of their formation is similar to the corresponding benzene derivatives.

816. We may always expect numerous substitution products in the benzene compounds, and frequently may arrange them in heterologous series containing the same nucleus, but which replace COOH (acid) for COCl (chloride), or $CONH_2$ (amide), or CH_2OH (alcohol), or CHO (aldehyde), etc.; as, *phthalic alcohol, or glycol*, $C_6H_4(CH_2OH)_2$, *phthalic chloride*, $C_6H_4(COCl)_2$, and *phthalic anhydride*, $C_6H_4{<}{CO \atop CO}{>}O$. Where there are two or more lateral groups, one may remain unchanged and give rise to mixed types, like the alcoholic benzoic acid, $(CH_2OH) \cdot C_6H_4 \cdot COOH$; and, finally, the nucleus may suffer further substitutions, and give rise to such compounds as nitro phthalic acid, $NO_2C_6H_3(COOH)_2$; nitro chlor-phthalic acid, $NO_2 \cdot C_6H_2Cl \cdot (COOH)_2$, etc.

The next page contains a selection of compounds taken from the "open" and the "closed" chains. The careful study of this table will enable the student better to comprehend the relations which exist among organic substances.

A COMPARISON BETWEEN THE

Fatty Series	and Aromatic Series.
CH_4, marsh gas.	C_6H_6, benzene.
CH_3Cl, methyl chloride.	C_6H_5Cl, phenyl chloride.
$(CH_3)'$, methyl.	$(C_6H_5)'$, phenyl.
CH_3NH_2, methyl amine.	$C_6H_5NH_2$, phenyl amine.
CH_3CN, methyl cyanide.	C_6H_5CN, phenyl cyanide.
$CH_3 \cdot CH_3$, ethane, di-methyl.	$C_6H_5CH_3$, toluene, methyl-phenyl.
$(CH_3 \cdot CH_2)'$ ethyl, $(C_2H_5)'$.	$(C_6H_5CH_2)'$ benzyl, $(C_7H_7)'$.
$CH_3 \cdot CH_2OH$, ethyl alcohol.	$\begin{cases} C_7H_7OH, \text{ cresol.} \\ C_6H_5 \cdot CH_2OH, \text{ benzyl alcohol.} \end{cases}$
CH_3CHO, aldehyde.	C_6H_5CHO, benzaldehyde.
CH_3COOH, acetic acid.	C_6H_5COOH, benzoic acid.
CH_3COCl, acetyl chloride.	C_6H_5COCl, benzoyl chloride.
$(CH_3CO)'$ acetyl, $(C_2H_3O)'$.	$(C_6H_5CO)'$ benzoyl, $(C_7H_5O)'$.
$(C_2H_3O)_2O$, acetic anhydride.	$C_7H_5O)_2O$, benzoic anhydride.
$C_7H_7 \cdot O \cdot C_2H_3O$, benzyl acetate.	$C_2H_5 \cdot O \cdot C_7H_5O$, ethyl benzoate.
$CH_3 \cdot CONH_2$, acetamide.	$C_6H_5CONH_2$, benzamide.
$(CH_3)_2CO$, acetone.	$(C_6H_5)_2CO$, benzophenone.
$CH_2Cl \cdot COOH$, chlor-acetic acid.	$C_6H_4Cl \cdot COOH$, chlor-benzoic acid.
CH_2NO_2COOH. ?	$C_6H_4NO_2COOH$, nitro-benzoic acid.
$CH_2NH_2 \cdot COOH$, glycocine.	$C_6H_4NH_2 \cdot COOH$, amido-benzoic acid.
$CH_3 \cdot CHOH \cdot COOH$, lactic acid.	$C_6H_4OH \cdot COOH$, salicylic acid.
$CH_2OH \cdot CH_2OH$, glycol.	$C_6H_4 : (CH_2OH)_2$, phthalic alcohol.
$CH_2(COOH)_2$, malonic acid.	$C_6H_4(COOH)_2$, phthalic acid.
$CH_3 \cdot CH : CH \cdot COOH$, crotonic acid.	$C_6H_5 \cdot CH:CH \cdot COOH$, cinnamic acid.
$CH_3 \cdot SO_2OH$, methyl sulphonic acid.	$C_6H_5 \cdot SO_2OH$, benzene sulphonic acid.

Hippuric acid, $C_7H_5O \cdot NH \cdot CH_2 \cdot COOH$, benzoyl glycocine.

Recapitulation.

The derivatives of the aromatic hydrocarbons which contain oxygen, include, among other compounds,—

(1) HYDROXIDES $(OH)'$. *The phenols*, which resemble tertiary alcohols, as C_6H_5OH, and also weak acids, forming salts, like sodium carbolate, C_6H_5ONa.

(2) DI-OXIDES $(O_2)''$. *The Quinones*, or double ketones $(CO)_2''$, including the important anthraquinone, $C_6H_4 : (CO)_2 : C_6H_4$.

(3) CARBOXYL derivatives, (COOH). *The Acids*, containing from one to six COOH radicals, and thereby forming mono-basic to hexa-basic acids.

(4) SECONDARY PRODUCTS from these by substitution of Cl, CN, OH, NO_2, SO_2OH, etc., for H in the carbon nucleus, which are also phenols, quinones, and acids.

(5) THE SALTS and ETHERS of the foregoing, with metals and alkyl radicals.

(6) THE REDUCTION PRODUCTS from acids, including *Alcohols*, $(CH_2OH)'$, *aldehydes*, $(CHO)'$, and *hydrocarbons* $(CH)_6$.

(7) COMPLEX SUBSTANCES, which may include radicals from any one of these, or from any one of the fatty series, bound to one or more oxy-benzene groups.

(8) THE NITRO (NO_2) and sulphonic (SO_2OH) derivatives are of great use in metathetical operations.

CHAPTER XXVIII.

AROMATIC SUBSTANCES CONTAINING NITROGEN.

817. When nitric acid acts upon organic bodies (1) it unites directly with basic substances, like aniline, forming salts; as, $C_6H_5NH_2HNO_3$, aniline nitrate. (2) It forms, with the alcohols, ethereal salts; as, $C_2H_5OH + HNO_3 = H_2O + C_2H_5NO_3$, ethyl nitrate. Both classes of these salts are easily decomposed by caustic potash.

(3) Dilute nitric acid is used as an oxidizing agent when only a moderate action is allowable, as in the preparation of phthalic acid.

(4) All aromatic compounds, when poured into strong nitric acid, form "nitro" substitution compounds, exchanging from one to three atoms of hydrogen in the *benzene nucleus* for an equal number of nitryl groups. At low temperatures, the product is ordinarily a mononitro derivative; as, $C_6H_5NO_2$. The di-, $C_6H_4(NO_2)_2$, and tri-, $C_6H_3(NO_2)_3$, nitro derivatives usually require the use of a mixture containing the strongest nitric acid with twice its volume of strong sulphuric acid.

When the substance has been dissolved by the acid, the entire mixture is poured into a large quantity of water to remove the excess of acid, etc. The nitro-derivatives settle out as yellow or reddish substances which are sometimes liquids, but more frequently crystallizable solids. These nitro compounds are not decomposed by boiling with potash lye, and, as a class, are far more stable than the nitro compounds of the fatty series.

Only a few have any direct application in the arts; but these are manufactured in enormous quantities in the preparation of the so called coal-tar dyes, aniline, alizarine, and their derivatives.

818. Mono-nitro benzene, $C_6H_5NO_2$, is also used under the name of the "essence of mirbane," as a substitute for the oil of bitter almonds. It is a poisonous, yellow fluid, which solidifies at 3°, and boils at 210°; sp. gr., 1.2.

The ordinary di-nitro benzene, $C_6H_4(NO_2)_2$, is the meta modification, a solid, easily soluble in hot alcohol, and crystallizing from such solutions in thin rhombic plates, which melt at 90°. The ortho compound melts at 118°, the para at 172°. It may be noted that para derivatives have generally the highest melting points.

Tri-nitro benzene, $C_6H_3(NO_2)_3$ (symmetrical), requires for its formation the mixture of the strongest acids, and long heating. It crystallizes from its alcoholic solution in white leaflets, which melt at 122°, and easily sublime.

These may be taken as types of the simple nitro derivatives. The methyl homologues, as nitro toluene, $C_6H_4 \cdot NO_2, CH_3$, nitro xylene, $C_6H_3 \cdot NO_2, (CH_3)_2$, etc., resemble them in their chemical reactions, but are not poisonous.

An enormous number of nitro compounds are known which contain, besides the NO_2 group, other radicals. The most important of these are the nitro-haloid, containing Br or Cl attached to the benzene nucleus; as, $Cl \cdot C_6H_4 \cdot NO_2$; the nitro phenols, which contain hydroxyl; as, $C_6H_4 \cdot NO_2, OH$, and the nitro-sulphonic acids, which contain the group SO_2OH, as nitro-phenol-sulphonic acid, $HO \cdot C_6H_3 \cdot NO_2, SO_2OH$.

819. Reducing agents convert nitro compounds to *amido* derivatives, in which "amidogen" $(NH_2)'$ replaces H in the benzene nucleus; as, $C_6H_5 \cdot NH_2$ = *amido benzene.* This reduction may be effected by the action of nascent hydrogen, obtained, *e. g*, by first mixing the nitro compound with strong HCl, and then adding tin or $SnCl_2$; as,

$$C_6H_5 \cdot NO_2 + 6HCl + 3Sn = 2H_2O + 3SnCl_2 + C_6H_5NH_2;$$ then (2),

$$C_6H_5 \cdot NO_2 + 6HCl + 3SnCl_2 = 2H_2O + 3SnCl_4 + C_6H_5 \cdot NH_2.$$

The product dissolves in excess of HCl to form hydrochlorides; as, $C_6H_5 \cdot NH_2HCl$.

In di- or tri-nitro derivatives, a partial reduction results in the formation of nitro-amido compounds; as, from $C_6H_4:(NO_2)_2$ may result $NO_2 \cdot C_6H_4 \cdot NH_2$.

820. The first of these amido compounds is ANILINE, or *phenylamine*, $C_6H_5NH_2$. The higher members of this series, toluidine, $CH_3 \cdot C_6H_4$, NH_2, etc., are metameric with the series of amines derived from the chlorides of the aromatic alcohols by the action of ammonia; as, $C_6H_5CH_2Cl + NH_3 = HCl + C_6H_5CH_2NH_2 =$ *benzyl amine*, which, however, contain the NH_2 group in the *lateral* chain.* The benzylamine series are freely soluble in water, and yield solutions which resemble those of the caustic alkalies. The members of both series are strong bases, and unite directly with acids to form salts, like those of ammonia. The members of the aniline series are but sparingly soluble in water. Their salts yield, by treatment with nitrous acid, "azo" and "diazo" compounds, p. 453; as, $C_6H_5 \cdot NH_2, HNO_3 =$ *aniline nitrate* $+ HNO_2 = 2H_2O + C_6H_5 \cdot N_2 \cdot NO_3 =$ *diazobenzene nitrate.*

Aniline is so named because it was first derived from indigo (Arabic, *Annil*). It is now manufactured in enormous quantities by reducing mono-nitro benzene with iron filings and acetic acid. The aniline salt which forms is decomposed by chalk, and the aniline distilled off by the aid of steam.

Aniline is a colorless liquid, which gradually becomes brown when exposed to the air; sp. gr., 1.036; solidifying in freezing mixtures, then melting at —8°, and boiling at 184°. It dissolves readily in alcohol, and in about 32 parts of water at 16°. This solution (1) colors

*The series of pyridine bases, page 461, contain pseudo isomers of these; as, *picoline*, $NC_5H_4 \cdot CH_3$.

a pine shaving yellow, (2) forms with a few drops of calcium hypochlorite, a purple violet color, *mauve.*

Aniline enters into a great variety of compounds:

I. By direct addition, (*a*) *with acids* to form salts which are generally soluble in water; as, $(C_6H_7N)_2H_2SO_4$, *aniline sulphate;* (*b*) with *certain metallic salts* to form double salts, like the *platinochloride,* $(C_6H_7N)_2PtCl_4$.

II. (*a*) By substitutions in the amido group *with alkyl radicals* by heating aniline with methyl iodide, etc., forming secondary and tertiary derivatives, like *methyl aniline,* $C_6H_5NHCH_3$, and, $C_6H_5N(CH_3)_2$, di-methyl aniline, etc. It is worth while to notice that these compounds, when heated strongly in closed vessels, are converted to the primary bases, which are isomeric with them, methyl aniline becoming *toluidine,* $CH_3 \cdot C_6H_4 \cdot NH_2$, and di-methyl aniline becoming, $(CH_3)_2 : C_6H_3 \cdot NH_2$, *xylidene.*

(*b*) *The anilides* are generally obtained by the action of an acid chloride upon aniline; as, C_2H_3OCl, acetyl chloride $+ C_6H_5NH_2 = HCl + C_6H_5 \cdot NH \cdot C_2H_3O =$ *acetanilide.* These are stable bodies, decomposed only after long heating with potash lye. Acetanilide forms colorless laminæ, which melt at 112°, and volatilize at 295°.

III. By substitution within the benzene nucleus by which monovalent radicals, like Cl, Br, NO_2, SO_2OH, replace from one to five hydrogen atoms, forming compounds, like the three mono-chlor anilines, $C_6H_4.Cl,NH_2$, the three mono-nitro anilines, $C_6H_4 \cdot NO_2NH_2$. These changes are effected in various ways, frequently by the direct action of Cl, Br, and of the fuming acids upon aniline. The basic character of aniline disappears either wholly or in part with the entrance of these negative radicals.

IV. Finally, aniline derivatives have been described which represent two or more of these groups.

The methyl derivatives of aniline are its homologues *toluidine,* $CH_3 \cdot C_6H_4 \cdot NH_2$; *xylidine,* $(CH_3)_2 : C_6H_3 \cdot NH_2$; *mesidine,*

$(CH_3)_3 : C_6H_2 \cdot NH_2$, etc., including their numerous isomers. They are formed by reduction of the nitro derivatives of their hydrocarbons, and exhibit analogous properties to those of aniline.

821. THE AZO AND DIAZO COMPOUNDS contain two nitrogen atoms, $N \cdot N$, linked together, and are named from *azote*, the French word for nitrogen. The following are examples of the structural formulæ of both.

Azo.		Diazo.	
$\begin{array}{l} C_6H_5 \cdot N \\ \qquad \mid > O \\ C_6H_5 \cdot N \end{array}$	Azoxybenzene.	$\begin{array}{r} C_6H_5 \cdot N \\ \Vert \\ NO_3N \end{array}$	Diazobenzene nitrate.
$\begin{array}{l} C_6H_5 \cdot N \\ \qquad \Vert \\ C_6H_5 \cdot N \end{array}$	Azobenzene.	$\begin{array}{r} C_6H_5 \cdot N \\ \Vert \\ HO \cdot N \end{array}$	Diazobenzene hydroxide.
$\begin{array}{l} C_6H_5 \cdot NH \\ \qquad \mid \\ C_6H_5 \cdot NH \end{array}$	Hydrazobenzene.	$\begin{array}{r} C_6H_5 \cdot NH \\ \mid \\ H \cdot NH \end{array}$	Phenyl hydrazin.

The azo compounds are intermediate between the nitro and amido derivatives of the aromatic hydrocarbons, and may be obtained by the partial reductions of the former, or by corresponding oxidations of the latter. For example, if sodium amalgam is added to a solution of nitro benzene, $2(C_6H_5NO_2)$, in alcohol, there will be produced in succession, azoxybenzene, $C_{12}H_{10}N_2O$; azobenzene, $C_{12}H_{10}N_2$; hydrazobenzene, $C_{12}H_{12}N_2$; and, finally, aniline, $2(C_6H_7N_2)$. The hydrazo compounds are colorless; the azo and azoxy, red or yellow. Only the azo compounds can be distilled without decomposition; all these yield substitution products with Cl, HNO_3, etc.

822. The diazo compounds are unstable bodies, often violently explosive when heated or struck, and very readily breaking up under the influence of various reagents. Diazo salts are produced when nitrous acid is made to act upon salts of those amido derivatives which contain the NH_2 group in the benzene nucleus; as,

$$C_6H_5 \cdot NH_2,\ H_2SO_4 = \text{aniline sulphate} + HNO_2 =$$
$$2H_2O + C_6H_5 \cdot N_2 \cdot HSO_4 = \text{diazo benzene sulphate.}$$

Great attention has recently been paid to these compounds, both by reason of the easy substitutions they admit, and for the brilliant and durable dyes produced by their various combinations.

As examples of these we may study the diazobenzene sulphate. (1) If boiled with water, it breaks up into $H_2SO_4 + \widehat{N}_2$, and $C_6H_5OH =$ *phenol.* (2) If treated with KI it forms *phenyl iodide*, C_6H_5I. (3) If heated with aniline, *diazo-amido benzene* forms $C_6H_5 \cdot N_2 \cdot NH(C_6H_5)$, which is gradually converted in the presence of a small amount of an aniline salt into its isomer, $C_6H_5 \cdot N_2 \cdot C_6H_4NH_2 =$ *amido azobenzene*, which is the dye known as *aniline yellow.*

Naphthylamine, $C_{10}H_7NH_2$, yields analogous products. (1) When heated with HNO_3 it forms di-nitro naphthol, whose sodium salt, $C_{10}H_5(NO_2)_2ONa$, is the brilliant *naphthalene yellow.* (2) On passing NO_2 into its warm alcoholic solution, an amido-azo naphthaline forms, which, on subsequent heating with additional naphthylamine, forms $C_{10}H_7 \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_7$, which yields the dye known as *magdala red.*

823. The aromatic hydrazins are bases, slightly soluble in water, easily in alcohol, and are either solids, having a low melting point, or are oily liquids. They are obtained by reduction of the diazo compounds. Nascent hydrogen reduces diazo-amido-benzol to aniline and phenyl hydrazin; thus,

$$C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5 + H_4 = C_6H_5NH_2 + C_6H_5NH \cdot NH_2.$$

Phenyl hydrazin, $C_6H_8N_2$, is a colorless oil, solidified by cold to tabular crystals. It is easily oxidized, and is, therefore, a good reducing agent. When added to Fehling's solution, it precipitates even without warming, the red Cu_2O, and is changed to aniline and benzene. This test may be used for other hydrazins, and also indirectly for the diazo compounds from which they may be formed. The nitroso hydrazins obtained by treating hydrazin salts with KNO_2, when mixed with any phenol and strong H_2SO_4, produce a series of fine colors,—brown, green, and finally blue.

Aniline Dyes.

824. The crude aniline, which is used in making aniline colors, contains a large percentage of para and ortho toluidine, $CH_3 \cdot C_6H_4 \cdot NH_2$. The red dyes can not be made from pure aniline. The first discovered of these dyes, *Mauve*, is prepared by oxidizing aniline sulphate with potassium bichromate. It contains the base *mauvein*, $C_{27}H_{24}N_4$, which, when united with various acids, yields the purple noticed in testing for aniline with chloride of lime.

The most important of these red dyes is made by heating crude aniline with arsenic acid (As_2O_5) to 140°. On dissolving the residue in dilute hydrochloric acid, and adding common salt, $C_{20}H_{19}N_3$, HCl, *rosaniline hydrochloride*, precipitates. This salt, known as *fuchsine*, on being dissolved in hot water, yields, on the addition of ammonia, a colorless precipitate of $C_{20}H_{21}N_3O$, which is generally considered as the hydrate of the base ROSANILINE, $C_{20}H_{19}N_3$, which was, perhaps, formed thus:

$$(C_6H_5NH_2)\,\textit{aniline} + 2(CH_3 \cdot C_6H_4 \cdot NH_2)\,\textit{toluidine} + O_3 =$$

$$3H_2O + 2(C_6H_4 \cdot NH_2) \begin{array}{l} :C \cdot C_6H_3 \cdot CH_3 \\ \quad \diagup \\ NH \end{array} = \textit{rosaniline.}$$

Other salts of rosaniline, with HNO_3 and $C_2H_4O_2$, are also sold as fuchsine, and are obtained in splendid gold-green crystals, readily soluble in alcohol to a beautiful red color. They dye wool and silk red without the addition of mordant (1 part fuchsine to 200 wool). Numerous interesting and valuable dyes have been prepared from rosaniline salts; as,

Aniline blue, $C_{20}H_{16}(C_6H_5)_3N_3HCl$, by heating fuchsine with excess of aniline.

Hofmann's violet, $C_{20}H_{16}(C_2H_5)_3N_3HCl$, by heating an alcoholic solution of fuchsine with ethyl iodide.

Aniline green, $C_{20}H_{14}(CH_3)_5N_3HCl$, by heating fuchsine with methyl iodide and methyl alcohol.

Fuchsine, warmed with sulphuric acid, yields sulphonic acids.

The mono sulphonic acid, when converted to its sodium salt, is the *Nicholson's blue*, $C_{38}H_{30}N_3SO_2ONa$, used in wool dyeing.

Aldehyde green, $C_{22}H_{27}N_3S_2O$, is formed by reducing aniline blue sulphonic acids by aldehyde.

Aniline black, $(C_{30}H_{25}N_5)$, forms when aniline hydrochloride is oxidized by potassium chlorate in presence of certain metallic salts, as $CuCl_2$. The metals appear to act as "carriers of oxygen," being alternately reduced and oxidized. The best blacks are obtained with salts of vanadium, one part of vanadium sufficing for 270,000 parts of the aniline salt.

The Indigo Group.

825. The juices of many plants contain a colorless glucoside, named *indican*, which decomposes when boiled with dilute acids into a sweetish substance, *indiglucin*, and *indigo blue;* thus, $2(C_{26}H_{31}NO_{17})$ *indican* $+ 4H_2O =$ $6(C_6H_{10}O_6)$ *indiglucin* $+ C_{16}H_{10}N_2O_2$, *indigo blue.* The indigo of commerce is prepared from the *Indigofera*, etc., by macerating their leaves in water, whereby a fermentation is set up which decomposes the indican, and also yields indigo white, $C_{16}H_{12}N_2O_2$, which dissolves. The liquid is then drawn off into shallow vessels, and is brought by stirring and beating into contact with the air as much as possible. This oxidizes the indigo white to indigo blue, which is allowed to settle, and is then washed and dried.

Baeyer has succeeded in the synthetical preparation of indigo blue. His actual process consists (1) in converting toluene to cinnamic acid (p. 443); (2) nitrating this to orth-nitro cinnamic acid, $C_6H_4 \cdot NO_2 \cdot CH : CH \cdot COOH$; (3) forming by action of bromine, $C_6H_4NO_2 \cdot CHBr \cdot CHBr \cdot COOH$, ortho-nitro-dibrom-cinnamic acid. (4) When this is treated with sodium hydroxide, and the product decomposed by an acid, ortho-nitro phenylpropionic acid forms $C_6H_4NO_2 \cdot C ⋮ C \cdot COOH$. (5) This, when reduced by nascent hydrogen or glucose, yields indigo blue.

$$C_6H_4 < \begin{array}{c} CO \cdot C \cdot NH \\ \quad \| \\ NH \cdot C \cdot CO \end{array} > C_6H_4.$$

826. Indigo blue is quite insoluble in water or alcohol, but dissolves without decomposition in concentrated sulphuric acid, forming, in the first instance, indigo monosulphonic acid, $C_{16}H_9N_2O_2(SO_2OH)$, but passing, on warming, into $C_{16}H_8N_2O_2(SO_2OH)_2$, sulphindigotic acid. This may be completely removed from its dilute solutions by clean white wool (Berlin blue). Its potassium salt is a valuable blue dye sold as *indigo carmine.*

Reducing agents in the presence of alkaline liquids convert indigo blue to *indigo white*, $C_{16}H_{10}N_2O_2 + H_2 = C_{16}H_{12}N_2O_2$, which dissolves, but may be precipitated in white flocks by neutralizing with an acid. These are rapidly reconverted to the blue on oxidation. Woolen fabrics, steeped in such alkaline solutions, absorb the coloring matter, and afterwards, on exposure to the air, are dyed of a permanent blue by the formation of indigo blue within the tissue.

Oxidizing agents convert indigo blue to *isatin*,

$$C_{16}H_{10}N_2O_2 + O_2 = C_{16}H_{10}N_2O_4, \text{ or } 2\left(C_6H_4<^{CO}_{NH}>CO.\right)$$

If the oxidizing action is carried too far other products are formed. For example, with $H_2O + Cl$, etc., *chlorisatin*, $C_8H_4ClNO_2$, *di-chlorisatin*, $C_8H_3Cl_2NO_2$, etc. Isatin dissolves freely in hot water, and crystallizes on cooling in yellowish-red prisms. The solution in alcohol colors the skin yellow and produces with it a persistent disagreeable odor.

Reducing agents (as P in PCl_5) may reconvert isatin to indigo blue, but usually they act by adding hydrogen. Nascent hydrogen in acid liquids produces *isatyde*, $C_{16}H_{12}N_2O_4$; in alkaline liquids, *dioxindol*, $C_{16}H_{14}N_2O_4$; then *oxindol*, $C_8H_7NO_2$, which, when heated with powdered zinc, yields *indole*, $C_8H_7N = C_6H_4<^{CH}_{NH}>CH$; and *skatole*, C_9H_9N. Both of these are ill-odored compounds which also occur in human excrement, and may be obtained from albumin by melting with KHO, or, better, by digestion with the pancreatic juice. So also, in the urine of mammals, a substance similar to indican sometimes occurs which colors the liquid blue on exposure to the air.

827. Several groups of the dye-stuffs have been mentioned in the preceding pages. The student will notice

(1) that the parent substances are colorless, or nearly so, as phenol, benzene, aniline; (2) that the tinctorial power enters with certain groups, as NO_2 in picric acid or CO in alizarine; (3) that other complex groups, like the tri-phenyl methane, $(C_6H_5)_3CH$, in fuchsine, are also required as "salt builders;" (4) that frequently the free base is also colorless, as in rosaniline, and that the dye-stuff is either manifested only in salts, or becomes intensified when they are formed; (5) that substances of similar composition exhibit similar colors, as rosaniline and rosolic acid; picric acid and trinitraniline.

828. The first of the coal-tar colors, *mauve*, was discovered in 1856, and has been followed by a large number of brilliant dyes, which have largely supplanted those then in use. The latter are either of inorganic origin as Scheele's green, or are derived from certain plants or from the animals that feed upon them. Many of the vegetable colors are so delicate and evanescent that they can not be employed in the arts; such, for example, is the *chlorophyll, or leaf-green.* This is found, together with protoplasm, in all the growing cells of plants exposed to sunlight, and appears to contain a blue coloring matter (*cyanine*), a yellow (*xanthine*), and a trifling amount of iron, but its chemical composition is unknown.

The vegetable dye-stuffs are generally produced from colorless glucosides, which are decomposed by fermentation, or by boiling with dilute acids, as already mentioned in the preparation of indigo and alizarine. The coloring matters thus obtained are themselves frequently almost colorless, and first take on a decided color when treated with certain re-agents known as mordants.

829. Besides the dyeing materials already considered the following require mention, and are placed here, although they do not contain nitrogen:

Anatto, obtained from the fruit of *Bixa Orelana,* as an orange

paste, is used in coloring butter and cheese. It contains *bixine*, $C_{28}H_{34}O_5$.

The orange-yellow, *saffron*, comes from the dried flowers of *crocus sativa*, as a glucoside of an agreeable odor. It contains *crocine*, $C_{16}H_{18}O_6$.

The safflower, *carthamus tinctorius*, contains, $C_{24}H_{30}O_{15}$, a yellow dye, soluble in water and a red dye, $C_{14}H_{16}O_7$, *carthamine*, which is used as a cosmetic.

Turmeric is extracted from the roots of the *curcuma longa*, by boiling with benzene. The coloring matter is, $C_{14}H_{14}O_4$, *curcumine*, which dissolves in alkalies with a brownish-red color. Turmeric paper is prepared from its solution in alcohol. When this is moistened with boracic acid, and then dried, it becomes orange-red, which changes to blue on adding an alkali.

Fustic is a yellow dye made from the wood of the *morus tinctoria.* It contains morine, $C_{12}H_{10}O_6$, and maclurine, $C_{13}H_{10}O_6$. The alcoholic solution of each is colored green by ferric chloride.

Brazil wood is employed in making red ink. It contains *braziline*, $C_{16}H_{14}O_5 + H_2O$, which is of a pale amber color, becoming a red upon oxidation, or when dissolved in alkalies.

The Logwood extract is made from the heartwood of the *Hæmatoxylon campechianum.* Its coloring power is due to *hæmatoxyline*, $C_{16}H_{14}O_6$, $3H_2O$, which, when first prepared, is quite colorless, but reddens in the sunlight. It dissolves in ammonia with a purple-red color, which rapidly darkens from the formation of *hæmateine*, $C_{16}H_{12}O_6$. The solution of logwood extract yields a red lake with alum solution, a dark violet lake with ferric salts, and a deep black with potassium chromate. These are extensively used in inks, and in producing browns and blacks upon cotton.

The cochineal and lac dyes are due to insects of the coccus family. The former contains carminic acid, $C_{17}H_{18}H_{10}$, which is a glucoside, yielding carmine red, $C_{11}H_{12}O_7$, soluble in water and alcohol. The commercial *carmine* of this is a lake, prepared by boiling the pulverized insects with water and precipitating with alum. The ammoniacal solution is used as a red ink.

The famous royal purple of the ancients was obtained from molluscs of the murex tribe.

830. The art of the dyer consists partly in imparting to a fabric the color desired, and partly in rendering it *fast;* that is, insoluble, so as not to be destroyed by washing. Some fibers, notably wool and silk, absorb

nitrogenous coloring matters directly, and require only an immersion in the hot dye-beck. Tissues, like linen and cotton, must be first *mordanted*,—that is, treated with solutions of the salts of tin, iron, alumina, etc.,—and afterwards be soaked in the alkaline solutions of the coloring matters employed. This treatment produces within the fiber of the cloth a *lake*, which has a color due partly to the dye-stuff, and partly to the mordant, and which is fixed by "ageing." This is attained by exposing the cloth either to the air or in chambers filled with steam. In some dyes, the color is made by purely chemical reactions; thus, if a piece of cloth is soaked in a solution of ferric chloride, and afterwards in one of potassium ferrocyanide, Prussian blue will be formed, and impart a fast-blue tint to the fabric.

831. The art of the calico-printer consists in producing, upon the natural white of bleached and cleansed cotton goods, patterns in one or more colors. If but one, he may produce a design in white or the converse by printing it before dyeing (I) with "resists" (acids that decompose the mordants, citric, phosphoric, etc.), or (II), with "discharges" (substances that prevent the absorption of the dye, as soap or grease, or that bleach it, as copper acetate in indigo printing); but (III), the usual process, known as the *madder style*, and also applicable for many shades and colors, consists (1) in printing the design upon the cloth by a sufficient number of engraved rollers, each smeared with the appropriate mordant, previously thickened by starch or gum. (2) The excess of the mordant is now removed by "cleansing" with hot water and cows' dung, or dung substitutes, like acid sodium phosphate or arseniate. (3) The goods are now boiled in a large vat containing the dye-stuff suspended or dissolved in water, and then (4), washed to remove the dye from the unmordanted portions. (5) The goods are now finished by "ageing."

Organic Bases.

832. The pyridine bases, $C_nH_{n-5}N$, are produced whenever complex nitrogenous compounds are subjected to dry distillation. They are, for the most part, bitter, poisonous substances, having a peculiar, penetrating odor. Pyridine, C_5H_5N, which is the first of the series, may be represented by a closed chain, $CH\left\langle\begin{matrix} CH-CH \\ CH=CH \end{matrix}\right\rangle N$, in which a single nitrogen atom has replaced one methenyl group, CH, of benzene. The homologues, as Picoline, C_6H_7N; lutidine, C_7H_9N; collidine, $C_8H_{11}N$, succeed each other by the increment, CH_2, as in the case of the benzene ring, and form a series of *nitrile* bases which are metameric with the amido-bases of the aniline series. About a dozen of these bodies are known, but the chief interest that attaches to them results from the theory which supposes that they represent the structure of some of the alkaloids, as the amine and imine compounds do the remainder.

833. The alkaloids are very important nitrogenous compounds, which always exhibit a basic character, and, like NH_3, unite directly with acids to form crystallizable salts, soluble in water. The free alkaloids, which are precipitated when such solutions are neutralized by alkalies, or by alkaline bicarbonates, are sparingly soluble in water, but dissolve, with differences of solubility, in alcohol, amyl alcohol, chloroform, ether, etc. Various reagents produce insoluble compounds when mixed with the alkaloids. Such are solutions of tannin and solutions of iodide of potassium containing I or HgI_2, etc. Generally speaking, the alkaloid may be regenerated from these by soda lye, but sometimes the compound requires previous treatment with sulphurous acid. It is not unusual to find several alkaloids in the same plant, and their complete separation is often a tedious labor.

The alkaloids and their salts are characterized by a bitter taste, and by their energetic action upon the animal economy. Very many are important medicines, and others are among the most active poisons known.

834. Most alkaloids are solids, and can not be distilled without decomposition. *Only three* are easily volatile; viz, conine, nicotine, sparteïne.

Conine, $C_8H_{14}NH$, obtained from the seeds of the *conium maculatum*, as a pungent, poisonous liquid, of stupefying odor; sp. gr., 0.84; boils, 170°. It behaves as an imide base, and may be oxidized to normal butyric acid. It is the noted "hemlock poison" of Socrates.

Nicotine, $C_{10}H_{14}N_2$, is found combined with malic acid in tobacco leaves (from 0.7 to 7%; Cuba tobacco containing much less than Virginia), and may be prepared by (1) soaking the leaves in dilute sulphuric acid, (2) distilling the concentrated extract with KHO. It is a colorless, poisonous liquid, which becomes brown on exposure to the air, having the disagreeable odor of rank tobacco; sp. gr., 1.02; boils at 247°. When tobacco is burned,—*i. e.*, smoked,—it yields, besides the undecomposed nicotine, other products, CH_4, C_2H_6, etc., and a number of pyridine bases, collidine, etc., scarcely less poisonous than itself.

Sparteïne, $C_{15}H_{26}N_2$, exists in the broom, *spartium scoparium*, and may be obtained from it as a bitter narcotic fluid, which, like nicotine, is a nitrile base.

835. The other alkaloids are non-volatile. Opium, the dried juice which has exuded from incisions made in the nearly ripened seed capsules of the poppy, *papaver somniferum*, is a complex mixture from which sixteen different alkaloids have been obtained, besides a variety of waxes, etc., and meconic acid, $C_7H_4O_7$, $3H_2O$. These alkaloids may be obtained in colorless rhombs and prisms, somewhat heavier than water, which are nearly all fusible at between 50° and 220°. Their solutions are, with

one or two exceptions, either optically inactive or lævo-rotatory. The most important are —

Morphine,	$C_{17}H_{19}NO_3$.	Papaverine,	$C_{21}H_{21}NO_4$.
Codeine,	$C_{18}H_{21}NO_3$.	Narcotine,	$C_{22}H_{23}NO_7$.
Thebaine,	$C_{19}H_{21}NO_3$.	Narceine,	$C_{23}H_{29}NO_9$.

When opium is digested with warm water, most of its alkaloids pass into solution. From such solutions the meconic and sulphuric acids present may be removed by barium chloride, and (2), on concentrating the filtered liquid, the hydrochlorides of morphine and codeine first crystallize out, and may be separated by ammonia in which only the codeine is soluble. (3) The mother liquor is mixed with ammonia, which precipitates all the others except narceine. (4) This precipitate is boiled with alcohol to dissolve out the thebaine, then with potash to extract the papaverine, leaving behind the narcotine.

Good Smyrna opium contains about ten per cent of morphine, but the amount is variable — from 4% to 24%. The narcotine is generally less than one fifth of this, and the remainder of the alkaloids are found in minute quantities. The peculiar physiological action of opium depends upon the joint effect of all of its active constituents. Nearly all, except papaverine, are considered poisonous. Morphine, narceine, and codeine are the chief pain-allaying and sleep-producing constituents. Thebaine is pain-allaying but not sleep-producing, and is the most active poison of the group; and narcotine is reckoned of little value in medicine.

Morphine, $C_{17}H_{19}NO_3 + H_2O$, crystallizes in rhombic prisms, which are soluble in 1000 parts of cold water, and readily in solutions of the fixed alkalies. The usual salts are the hydrochloride, $C_{17}H_{19}NO_3$, $HCl + 3H_2O$, and the sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$, which crystallize in slender needles, easily soluble in water and in alcohol. Morphine is readily oxidized to oxy-di-morphine, $C_{34}H_{36}N_2O_6$, and hence acts reducing.

TESTS. It reduces $K_3FeC_3N_6$, etc., I_2O_5 (with separation of free iodine), and produces a characteristic blue when mixed with neutral Fe_2Cl_6.

Codeine, $C_{18}H_{21}NO_3 + H_2O$, is methyl morphine, and when heated with HCl yields apomorphine, $C_{17}H_{17}NO_2$, and methyl chloride. It resembles morphine in its therapeutical properties, but is soluble in ether and in 80 parts of water, and does not produce a blue coloration with Fe_2Cl_6.

Narcotine, $C_{22}H_{23}NO_7$, yields to HCl, three methyl groups, one after the other becoming finally nor-narcotine, $C_{19}H_{17}NO_7$, and is further characterized by breaking up when boiled with water or weak alkalies into *meconine*, $C_{10}H_{14}O_4$, an acid anhydride occurring naturally in opium and a variety of other products.

836. Piperine, $C_{17}H_{19}NO_3$, constitutes nearly nine per cent of the East Indian peppers. It is almost tasteless because so slightly soluble in water; its alcoholic solution has a sharp, peppery taste. When this solution is heated with KHO, it forms *piperic acid*, $C_{12}H_{10}O_4$, and *piperidine*, $C_5H_{11}N$.

Piperidine is an alkaline fluid, smelling strongly of pepper and ammonia, boiling at 106°, and converted by boiling with H_2SO_4 into *pyridine*, but it is also formed from pyridine by the action of Sn + HCl.

837. Sinapine, $C_{16}H_{23}NO_5$, is found in white mustard seeds, combined with CNSH. On boiling ground mustard with alcohol, the sinapine sulphocyante dissolves, and may be crystallized in fine needles, which melt at 130°. The free base is exceedingly unstable, and is decomposed on boiling into sinapic acid, $C_{11}H_{12}O_5$, and neurine, $C_5H_{15}NO_2$ (page 386).

838. The chinchona bases are the alkaloids found in the bark of the chinchona trees of Peru. Only quinine and chinchonine are employed in medicine, the former being held in almost universal repute as a tonic and febrifuge.

The yellow, or Calisaya bark, contains the largest percentage

(3%) of quinine, the grey, or Huanaco, bark is especially rich in chinchonine (2%). The red bark contains both. The alkaloids exist in these, as salts of quinic and quino-tannic acid, and are extracted (1) by treating the ground bark with dilute HCl, filtering, and then precipitating the bases with lime. (2) This precipitate is boiled with alcohol, exactly neutralized by H_2SO_4, and evaporated. Quinine sulphate first crystallizes out, then chinchonine sulphate. The mother liquor retains the salts of the other bases, among which are *quinidine* and *chinchonidine*, isomers of the other two.

Quinine, $C_{20}H_{24}N_2O_2 + 3H_2O$, is precipitated from its salts by alkalies, as a white powder, soluble in 1670 parts of water, but easily in ether and chloroform. The sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$, is the salt commonly used in medicine, soluble in about 800 parts of water, but soluble in 11 parts of water containing dilute H_2SO_4, due to the formation of the acid salt,

$$C_{20}H_{24}N_2O_2,\ H_2SO_4 + 7H_2O = \textit{quinine bisulphate.}$$

All solutions containing quinine are characterized by a bitter taste, and by a blue fluorescence. They yield when chlorine water is first added, and then ammonia, an emerald green color.

Quinidine resembles quinine in its medicinal properties, but is more easily soluble.

Chinchonine, $C_{19}H_{22}N_2O$, does not yield the same chemical reactions with quinine, but has some use as a substitute for quinine in medicine. It is less soluble than quinine, although its salts are more soluble in water and alcohol. It bears a close resemblance to its isomer, *chinchonidine*, which occurs together with quinidine in the last resinous mass obtained after the removal of the quinine and chinchonine sulphates, and sold as *quinoidine.*

When the sulphates of these four bases are heated to 135°, two other isomeric bases are produced, viz, *quinicine* and *chinchonicine.*

We now have two series of isomers, which are characterized by the deviations they severally produce in polarized light, viz:

$C_{20}H_{24}N_2O_2$.			$C_{19}H_{22}N_2O$.		
Quinine	(left)	—145°.	Chinchonidine	(left)	— 70.°
Quinicine	(right)	+ 44°.	Chinchonicine	(right)	+ 46.°
Quinidine	(right)	+ 237°.	Chinchonine	(right)	+ 226.°

All these, when distilled with dry potash, yield three bases of the formula $C_nH_{2n-11}N$; as, *chinoline*, C_9H_7N, which are isomeric with a series, *leucoline*, etc., obtained from coal-tar naphtha.

839. **The strychnos alkaloids** are found in the bark and roots of the strychnos plants, and especially in the seeds or beans of the *S. nux vomica* and the *S. St. Ignatii* (1.5%).

They are obtained (1) by boiling the crushed seeds in very dilute H_2SO_4; (2) concentrating the liquor, to which a little plumbic acetate is added, and (3), boiling with ordinary alcohol, and filtering hot. (4) To this is added magnesia, and the whole allowed to stand for a week. (5) Finally, this precipitate is boiled with alcohol, which removes both bases. On cooling, the *strychnine* first crystallizes out, and then the *brucine.*

Strychnine, $C_{21}H_{22}N_2O_2$, forms in white rhombic prisms, somewhat soluble in ordinary alcohol, $\frac{1}{107}$, and very sparingly in water. It imparts to these solutions an intensely bitter taste. When taken in small doses, $\frac{1}{30}$ grain, it is a valuable tonic, but it is also one of the most violent poisons known. Its effects are similar to those produced by tetanus. It dissolves in cold H_2SO_4 without change of color. This solution, oxidized with $K_2Cr_2O_7$, PbO_2, etc., gives characteristic colors; first, a bluish violet, then a red, and finally green.

Strychnine is entirely removed from its solutions by animal charcoal.

Brucine, $C_{22}H_{26}N_2O_4 + 4H_2O$, resembles strychnine in its physiological properties, but it is decidedly less

poisonous. It is sparingly soluble in cold water, but easily in alcohol. Strong nitric acid colors brucine to a fine and characteristic red color, which becomes, on warming, yellow, which is changed to a deep violet by reducing agents, like $SnCl_2$.

Curarine, $C_{18}H_{35}N$, is the active principle in the South American arrow poison, which is probably the dried juice of some strychnos-like plant.

The Ptomaïnes are a group of alkaloids, some of which are volatile and not poisonous, while others resemble strychnine both in their chemical reactions and in their poisonous properties. They are obtained from albuminoid substances, which have decomposed without free access to the air (canned meats? mouldy maize?), and hence are found in buried animal remains, and are said also to occur in fresh blood and egg albumin.

Eserine, or *physostigmine*, $C_{15}H_{21}N_3O_2$, is the resinous extract of calabar beans, easily melted and quite soluble in alcohol and cold water. It is readily oxidized, and is one of the most active poisons known. It produces a marked contraction in the pupil of the eye.

840. The atropine group contains several alkaloids of the formula, $C_{17}H_{23}NO_3$, which strikingly resemble each other. When boiled with strong KHO or HCl, they are converted to *tropic acid*, $C_9H_{10}O_3$, and $C_8H_{15}NO$, *tropine*, or its isomer. Conversely, the mixture of these substances, when boiled for some hours with dilute HCl, produces atropine.

(1) **Atropine** is identical with *daturine*, and is obtained from the *atropa belladonna* (deadly nightshade) or from the *datura stramonium* (thorn apple) by warming the seeds of these plants with dilute potash, and then shaking the mixture with chloroform. On evaporating this, redissolving in alcohol, and then diluting with water, the atropine separates in oily drops, which change to bright needles slightly soluble in water, and melting at 114°.

(2) The mother liquor above obtained, contains *hyoscyamine*, which is preferably prepared from *hyoscyamus niger* (henbane), which also contains a third isomer, *hyoscine*. The hyoscyamine forms in silky needles, easier soluble than those of atropine, and of a lower melting point, 108°.

All these are active poisons, and are characterized by strongly dilating the pupil of the eye.

841. Various other plants contain alkaloids peculiar to them. Among these are:

Pilocarpine, $C_{11}H_{16}N_2O_2$, is a poisonous base resembling nicotine. When heated by itself, or with HCl, it is changed to *jaborine*, a very strong base, which is also found in Jaborandi leaves. It is also poisonous, acting like atropine.

Solanine, $C_{42}H_{75}NO_{15}$, is a poisonous glucoside found in all the solanum plants, and readily obtained from the fresh buds of potatoes which have sprouted in the dark. It is resolved on boiling with dilute HCl into glucose and *solanidine*, $C_{26}H_{41}NO_2$. This alkaloid crystallizes in fine long needles, which melt at 200°, and may be in part sublimed. It is colored red by H_2SO_4.

The veratrum family of plants contain no less than seven alkaloids. The only important ones are *cevadine*, $C_{32}H_{49}NO_9$, until recently known as *veratrine* (which name is now given to $C_{37}H_{53}NO_{11}$), and *jervine*, $C_{26}H_{43}NO_2$. The first of these is characterized by producing, when taken into the nose, a most violent sneezing; when swallowed, it is a powerful emetic, and also a narcotic poison. Both it and the veratrine dissolve in H_2SO_4, with first a yellow and then a carmine-red coloration. Jervine so treated becomes finally emerald green.

Aconitine, $C_{33}H_{43}NO_{12}$, is obtained from the roots of the *aconitum napellus* (monk's hood) in rhombic tables, melting at 183°, and sparingly soluble in water. It has a peculiar prickling taste, and is exceedingly poisonous.

Colchicine, $C_{17}H_{19}NO_5$, is a yellow amorphous powder obtained from the meadow saffron, easily soluble in water, and melting at 140°. It has an intensely bitter taste, and is an active poison.

Emetine, $C_{28}H_{40}N_2O_5$, is the active principle of the ipecacuanha root. It is a medicine, valuable in small doses for bronchial troubles, but in larger, acts as a violent emetic, and is poisonous.

Recapitulation.

Among the aromatic compounds, which contain nitrogen, are:

I. The following classes of bases

as from benzene, ... C_6H_6.

(1) Amine, ... $C_6H_5NH_2$.

(2) Hydrazo, ... $(C_6H_5)_2(HN)_2$.

(3) Azo, ... $(C_6H_5)_2N_2$.

(4) Azoxy, ... $(C_6H_5)_2 \cdot N_2 \cdot O$.

(5) Diazo, ... $C_6H_5 \cdot N_2 \cdot Cl$.

(6) Hydrazin, ... $C_6H_5(NH)_2H$.

(7) Nitrile, ... C_6H_5CN.

These include a great variety of dye-stuffs, — aniline, rosaniline, naphthylamine, etc.

II. Products of destructive distillation, like the pyridine bases, C_nH_{2n-5}, and chinoline, C_nH_{2n-11}.*

III. The vegetable alkaloids. Some of these resemble the amine bases, some the pyridine, in their chemical structure.

IV. The glucosides which contain these alkaloids, as indican.

V. Other organic compounds containing nitrogen are the amides and amic acids (Chapter XXIV); and,

VI. The nitro (NO_2) and nitroso (NO), formed by substituting these radicals for hydrogen.

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* Another series, $C_nH_{2n-3}N$, is represented by pyrrol, C_4H_5N, which is also found in coal-tar.

CHAPTER XXIX.

VEGETABLE AND ANIMAL CHEMISTRY.

842. The molecular structure of most of the substances immediately connected in the chemical changes which take place in living plants and animals is practically unknown. A portion of these,—the starches, sugars, amides, etc.,—have been assigned to a provisional place in the chemical system, but there remain others which chemists have failed to classify. Among the most important of these are those brought together in this chapter.

843. The drugs used in medicine contain a number of active constituents which have not been satisfactorily grouped from the chemist's point of view. Among these are the so-called "*bitter principles*," which have a bitter taste, and are popularly regarded as tonics; such as the bitter of hops, $C_{16}H_{26}O_4$, of quassia wood, $C_{10}H_{12}O_3$, and of columbo-root, $C_{21}H_{22}O_7$.

Aloïn, $C_{17}H_{18}O_7$, the purgative principle of Barbadoes aloes, has a taste at first sweetish, and then intensely bitter. By prolonged action of HNO_3 it is converted to chrysammic acid, $C_{14}H_4(NO_2)_4O_4$, which is used as a dye.

Santonin, $C_{15}H_{10}O_3$, and *absinthiin*, $C_{20}H_{28}O_4$, found in certain species of wormwood, and *koussin*, $C_{31}H_{38}O_{10}$, from the kousso plant, are yellowish substances of very bitter taste, classed in medicine as anthelmintics.

Picrotoxin, $C_{15}H_{16}O_6 + H_2O$, is the poison of the cocculus indicus, intensely bitter, and a good reducing agent.

With these substances may be classed *lactucin*, a bitter substance found in lactucerin, $C_{20}H_{32}O_2$, the dried sap

of the lettuce, supposed to possess narcotic powers resembling that of opium.

Some glucosides are popularily named with these because of their bitter taste, as chiretin, salicin, phlorizin, and arbutin, but are not otherwise related. A few glucosides yield, besides glucose, a crystallizable body which might be reckoned with this group, as *æsculin*, $C_{15}H_{16}O_9$, found in the horse-chestnut bark, which yields *æsculetin*, $C_9H_6O_4$. Another is *quercetrin*, $C_{36}H_{38}O_2$, which contains *quercetin*, $C_{24}H_{16}O_{11}$, a yellow crystallizable substance.

On the other hand, a number of substances put into this group have neither taste nor odor. Such, for example, is $C_{10}H_{10}O_3$, *cubebin*, from the *piper cubeba; caryophyllin*, $C_{20}H_{32}O_2$, from cloves, and *gentisin*, $C_{14}H_{10}O_5$, from gentian roots. And with them a group of bodies which are spoken of as indifferent matters, in the sense that they are neither bases nor acids, as $C_{24}H_{30}O_7$, *athamantin*, from the *athamanta oreoselinum.*

Carotin, $C_{18}H_{24}O$, the coloring matter of the carrot, from which it may be obtained in red-brown cubes; of pleasant violet-like odor.

Cantharidin, $C_{10}H_{12}O_4$, is obtained from Spanish flies, potato-bugs, and other beetles, in rhombic tables which are insoluble in water. It is an active blistering agent and poison.

The Bile.

844. The bile of animals is the secretion of the liver, which collects in the gall-bladder. It is a mixture containing in solution a variety of substances, among which are fatty soaps, lecithins (p. 407), cholesterin (p. 433), certain pigments, and the sodium salts of the bile acids (§ 729).

The acids found in the bile of oxen are *glycocholic* and *taurocholic*, both of which yield, on boiling with dilute alkalies, the same decomposition product; viz, *cholic acid*, $C_{24}H_{40}O_5 + H_2O$.

This acid may be obtained in quadratic octahedrons, soluble in alcohol, and is decomposed, upon boiling with HCl, with formation of *dyslysin*, $C_{24}H_{36}O_3$ and $2H_2O$. These substances, when gently warmed with strong sulphuric acid and a little sugar, give a beautiful

violet red coloration, which is known as Pettenkofer's test" (§729). The acids are prepared (1) by treating fresh ox-gall for several days with HCl and ether; (2) then dissolving the resinous mass, which has formed, in boiling water, and (3), crystallizing.

Glycocholic acid separates out first in fine white needles, soluble in about 100 parts of cold water. The mother liquor contains *taurocholic acid*, also obtainable in silky needles. Both these acids have a sweetish-bitter taste, and give a foamy lather when shaken up with water. The second product of the decomposition of glycocholic acid is glycocoll (p. 384), or *glycocine*,

$$C_{26}H_{43}NO_6 + H_2O = C_{24}H_{40}O_5 + NH_2 \cdot CH_2 \cdot COOH,$$

and the second product of taurocholic acid is *taurine* (p. 386),

$$C_{26}H_{45}NSO_7 + H_2O = C_{24}H_{40}O_5 + NH_2 \cdot C_2H_4 \cdot SO_2OH.$$

Glycocine and taurine are present in the bile of most animals, not free, but in combination with cholic or a similar acid, and, together, forming sodium salts. Ox-bile contains rather more of glyco-cholic than of tauro-cholic acid. Pig's bile contains $C_{27}H_{43}NO_5$, *hyo-glycocholic* acid, with a little *hyo-taurocholic* acid. The acid of goose-bile is principally *cheno-taurocholic* acid, $C_{20}H_{49}NSO_6$.

The color of the bile varies from a golden-yellow in man, the greenish-brown of herbivora, to the bright-green of birds, and is due mainly to a reddish-brown pigment, *bilirubin*, $C_{32}H_{36}N_4O_6$, and a green pigment, *biliverdin*, $C_{32}H_{36}N_4O_8$. The first dissolves in alkaline liquids, with an orange-red color, which appears yellow when much diluted, as noticed in jaundice. This solution readily absorbs oxygen, and becomes green from the formation of biliverdin.

Gmelin's test is founded upon this property, and is made by adding to bile, sodium nitrate, and then pouring over this strong H_2SO_4. The nitrous acid which is evolved colors it first green, then blue, violet, red, and at last a yellow.

Certain intestinal concretions, found in Persian goats, and known as "Oriental Bezoar Stones," contain *lithofellic acid*, $C_{20}H_{36}O_4$, which gives Pettenkofer's test, and in other respects resembles glycocholic acid.

Protein Substances.

845. The protein or albuminoid substances are formed primarily in plants, and are stored up in plant tissues and organs, but especially in leaf buds and in seeds. The animals which feed upon these so change their external form, and assimilate them, that they become the essential constituents of the nutritive fluids of animals, and most of the soft solids of their organism,—flesh, tendons, etc. Nevertheless, the composition and chemical properties of these compounds are very much alike, whether derived from plants or from animals. In the living organism, they are found mixed with various other bodies (water, chlorides, phosphates, fats, etc.), so that it is an exceedingly difficult matter to obtain them sufficiently pure for accurate determination of their composition, or to obtain satisfactory formulæ for any of them. The results of analyses show an average percentage of C 53, H 7, N 15.8, S 1.4 (O 22.8 by difference), which corresponds to $C_{72}H_{118}N_{18}SO_{22}$.

It is possible that the differences in their properties are due to the presence of isomers or polymers of some protoplasmic substance as yet undiscovered. It is very evident that they must have a high molecular weight: (1) because they do not diffuse through membranes; (2) they are exceedingly prone to decomposition; and (3), yield an unusual number of decomposition products. Among these are gases, like CO_2, H_2S, and NH_3; amide bodies, such as glycocine, leucine, tyrosine, aspartic acid, and glutamic acid; the fatty acids and their aldehydes from formic to palmitic; also, oleic, lactic, and succinic acids; besides various aromatic compounds, as benzoic acid, phenol, indol, and skatol.

846. The albumins, soluble in water, are three: (1) *Albumin*, which is coagulated or rendered insoluble at the temperature of 72°; (2) *Casein*, which is only partially coagulated upon boiling, but completely upon the addition of acetic acid; (3) and the albumin of blood

plasma, which separates, as the insoluble *fibrin* upon exposure to the air. When once coagulated, these strongly resemble the insoluble albumins, *globulin*, *lardacein*, and the *derived albumins.*

847. All the albuminoids are soluble in dilute mineral acids, and in dilute solutions of the alkalies, and of certain salts, like NaCl. (1) They are precipitated therefrom by stronger acids and salt solutions, and by antiseptics, like the salts of Hg and Cu, by tannin, carbolic acid and alcohol, in white flocks (*coagulated albumin*), which, when dried, form a horny, semi-transparent, amorphous mass. (2) Heated by themselves in the air, they carbonize and emit an odor resembling that of burnt feathers. (3) Heated with moderately strong HNO_3, they change to *xanthoproteic acid*, an orange-yellow substance, which dissolves in alkalies with an orange-red color. (4) Heated with Millon's re-agent,* mercuric nitrate, they yield a fine red color.

848. The albumins, properly so-called, are found in the white of eggs, in the serum of blood, and in the juices of most vegetables. Both egg and blood albumin have an extensive use in calico printing, and in the preparation of albuminized paper for the use of photographers.

The globulins are soluble in dilute solutions of sodium chloride, but not in pure water. The animal globulins comprise: (1) *Vitellin*, which is a constituent of the yolk of hen's eggs; bodies similar to this are found in the chyle and in the crystalline lens. (2) *Myosin*, or flesh fibrin, which is found in the living muscle as a liquid; after death (in *rigor mortis*) it curdles rather than coagulates, since it may be readily extracted from finely-divided flesh by means of a dilute solution of NH_4Cl.

(3) The blood and all the serous liquids of the body

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*Prepared by digesting 1 part of Hg with 1 part HNO_3. and then adding $4H_2O$. The clear liquid which separates from the insoluble portion is the re-agent.

contain, not only serum-albumin, but also two modifications of globulin. These are known as the *fibrino-plastic substance* and *fibrinogen.* When the blood has been removed from a living animal, these two substances unite and form *fibrin*, which is the chief part of the *blood-clot.* This fibrin may be obtained as a white, stringy solid by beating freshly-drawn blood with twigs, and then washing with water. Fresh fibrin resembles dried albumin, but is more readily oxidized, decomposing hydric peroxide with evolution of oxygen, and is quickly dissolved by the gastric juice.

(4) **The plant globulins** are very similar to those of animals. Maize and peas contain both vitellin and myosin. Squash-seeds contain a large amount of the former, and white mustard-seeds are especially rich in the latter.

The gluten found in the cereals, and which may be obtained from wheat flour by kneading it with water until all the starch has been washed out, is a tough elastic substance of the utmost importance in bread-making. It is frequently called *vegetable fibrin*, but is really a mixture containing *gluten-fibrin*, *mucedin*, and *gliadin*, or *vegetable gelatin*, which are fibrin-like bodies that may be extracted from crude gluten by strong alcohol, leaving behind a fourth albuminoid, which is *gluten-casein.*

The animal caseins are found dissolved in milk by reason of the presence of an alkali, and hence they are spoken of as *alkali albuminates.* When this alkali is neutralized by an acid, as the lactic acid of sour milk, the casein separates out as a *curd.* The same change is effected by means of the ferment in calf-rennet, which is used in the manufacture of cheese.* It is probable that casein is a mixture of several albuminoids, inasmuch as the casein of cow's milk differs in some respects from that of other mammalia. An "artificial casein"

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*One part of this ferment, "*lab*," suffices for 800,000 parts of casein.

may be derived from egg or serum albumin by the prolonged digestion of either in caustic soda, and subsequent precipitation by acetic acid. This is not coagulable by rennet.

The vegetable caseins are alkali-albumins, which exist in peas and beans as *legumin;* in lupines and the kernels of stone fruits, as *conglutin;* and in the cereals, as *gluten-casein.*

All these forms of casein, when freshly precipitated and thoroughly washed, are insoluble in pure water, but are readily soluble in dilute alkalies, and reprecipitated therefrom by very dilute acids, as a snow-white powder, entirely free from "ash," of a decidedly acid reaction, and soluble in hot alcohol.

Cheese is the "ripened curd" of milk, containing more or less of the milk fats and salts. The ripening of cheese is due to a fermentation by which a portion of the albuminoid is decomposed with formation of certain products which give to old cheese its peculiar odor and taste.

The Chinese make a cheese from the pulp of ground peas, which is said to resemble very closely that produced from milk.

849. Albumin derivatives are formed (1) by the action of dilute alkalies upon the albuminoids, as already mentioned in artificial casein; (2) by dissolving any of those described in dilute acids, thereby forming acid albumins, or *syntonins.* On neutralizing the acid, these bodies are thrown down as flocculent, gelatinous bodies, insoluble in hot alcohol, but easily dissolved in alkalies, as alkali-albumins, and as easily reconverted to acid-albumins by acids.

(3) **Coagulated albumin** is also considered as a derived albumin. When obtained from albumin, globulin, fibrin, etc., by heating or by alcohol, it becomes difficultly soluble in dilute alkalies and acids, although soluble by prolonged digestion with acetic acid. It may

be converted into alkali-albumins by caustic soda, or into acid albumins by strong hydrochloric acid.

(4) **The peptones** are the products obtained by the digestion of the food albuminoids with the gastric and pancreatic juices. They are naturally mixtures of several decomposition products. Such of these as resemble albumin in percentage composition differ essentially in several important particulars. They are soluble in water, and are easily diffusible. Their aqueous solutions are not precipitated by heating with dilute acids, alkalies, nor by alkaline salts, but are coagulated by strong alcohol and by $HgCl_2$.

They are, therefore, the modified forms by means of which the various albuminoid substances enter into the nutritive fluids of the animal organism, and of course must exhibit differences due to the character of the food and the process by which the peptone is obtained for examination.

850. The soluble nitrogenous ferments have about the same percentage composition as the albuminoids. They are soluble in water, and are not precipitated upon boiling, although they lose their peculiar fermentative power thereby. No formula can be given for any one of them. The vegetable ferments are *emulsin* in the juice of almonds, *myrosin* in mustard seeds, and *diastase*, which is the ferment formed from gluten in the germination of seeds, and is an agent by which starch is changed to dextrin, and then to malt sugar. The animal ferments, *ptyalin* of the saliva, and *trypsin* of the pancreatic juice, have the same power when in alkaline solution.

The pepsin, which is the active ferment of the gastric juice of the stomach, converts all of the albuminoids into syntonins, and then into soluble peptones, etc. It acts most readily at 30°–40°, and is hindred by the presence of strong alcohol and the caustic alkalies. The pepsin sold by apothecaries is obtained by scraping the

mucous membrane of a pig's stomach, and afterwards drying the pulp so obtained.

With these ferments must undoubtedly be mentioned the poisons present in the venom of snakes, of rabies, and of glanders, and perhaps, also, other products of derived albumins.

The yeast-plant, the various forms of bacteria, and other bodies supposed to act as "disease germs," are organized plants or animals. They contain nitrogen, and require nitrogenous food for their support. They are known to multiply with marvellous rapidity, and to be destroyed by agents that coagulate albumin.

851. The hæmoglobins are the blood pigments of vertebrate animals, and may be obtained from the red corpuscles of arterial blood in fine rhombic crystals. These crystals are *oxy-hæmoglobin;* that is, they are hæmoglobin combined with oxygen, but this union is so feeble that the oxygen is given off when the warmed blood is brought into a Torricellian vacuum, and is re-absorbed on exposure to the air. Reducing agents, like ferrous salts, also convert oxy-hæmoglobin to hæmoglobin. This is very soluble in water, and greedily absorbs oxygen, becoming reconverted to oxy-hæmoglobin.

This substance is the carrier of oxygen to the body. The red or arterial blood, during its circulation, parts with its oxygen, and takes, in its place, the carbonic anhydride, which is a waste product of the tissues, and becomes the purple or venous blood. As this passes through the lungs, the reverse action takes place, carbonic anhydride is given off, and oxygen absorbed.

Certain gases, like carbonous oxide, form more stable compounds with the hæmoglobin, and prevent the absorption of oxygen, and, therefore, act as powerful poisons.

The composition of hæmoglobin must be exceeding complicated. The formula, $C_{600}H_{960}O_{179}N_{154}FeS_3$, has been proposed for it, which supposes a molecular weight of 13332, or nearly 7000 times that of hydrogen. It contains 0.42 per cent of iron. The amount of hæmoglobins in blood varies from 12.17% in women, to 13.45% in men.

Hæmatin, $C_{35}H_{34}FeN_4O_5$, is obtained by treating defibrinated blood with acetic acid. There first forms, *hæmatin acetate*, which may be obtained in microscopic crystals, which are sometimes regarded as test for blood in medico-legal cases. On neutralizing this acid solution with an alkali, the hæmatin falls in brownish flocks, which, on drying, becomes a bluish-black powder. It is a moderately stable substance, which, when heated strongly, leaves behind a residue of ferric oxide (7%).

The animal mucus, which is found in the glairy exudations of the mucous membranes, and in many secretions, bile, synovial liquor, saliva, etc., yields syntonin upon boiling with dilute mineral acids. The chief constituent of these substances is *mucin*, which is easiest obtained from edible snails. It is easily soluble in dilute alkalies, and precipitated from such solutions by alcohol, or by acetic acid.

Para-albumin, and the so-called *amyloid matter* or *lardacein*, are modified albumins produced in certain diseases.

852. The gelatins do not exist ready formed in the animal, but are manufactured from two varieties of protein substances, named collagen and chondrogen.

Collagen is found in the connective tissues,—skin, tendons, etc.,—and in that portion of the bone (*ossein*) which is not dissolved by dilute HCl. The dried air-bladder of the sturgeon (isinglass) is a variety of it. The formula, $C_{102}H_{149}N_{31}O_{38}$, represents very nearly the average composition of ossein.

Chondrogen is found in permanent cartilage, in the cornea of the eye, and in young bones previous to their hardening. It is probably a mixture containing mucin and a variety of collagen; but the glue (chondrin) that is made from it differs from ordinary glue made by boiling collagen, in some important particulars, having less adhesive power, and yielding little or no glycocoll upon decomposition.

Nevertheless, these substances agree in most of their properties. They putrefy readily when in the moist state, and yield leucine and other common products of decomposition. The putrefaction of collagen is prevented by tannin, as is splendidly exemplified in the conversion

of raw hides into leather. They are both quite insoluble in cold water, but dissolve in boiling water. This solution, upon cooling, sets into a soft jelly-like mass which is, when dried, the *gelatin* of commerce. The gelatin used for jellies, soups, etc., is made from selected materials with, perhaps, the addition of rock-candy. Printers' ink-rolls are mixtures of glue and molasses. The gelatin capsules of the apothecaries are made from gelatin, gum arabic, sugar, and glycerol. The addition of the two latter substances impart a great degree of flexibility to the gelatin.

853. The best glue is made from cuttings of hides, etc., and is dried at 25° in shallow trays, and finally upon wire netting. It is an amorphous, translucent substance of a light amber color, valuable because of its adhesive power when applied to wooden joinings. Placed in cold water, it does not dissolve, but swells up to three or four times its former volume. On warming this swollen mass it dissolves, but again gelatinizes upon cooling. Long boiling of glue destroys its valuable adhesive properties. The gelatinizing of glue may be prevented by the addition of acetic, or a very little nitric, acid to its aqueous solution, without perceptible loss of its adhesive properties (liquid glue).

When a solution of glue is mixed with potassium bichromate, and exposed to sunlight, it forms a solid mass insoluble in water. This property is applied in photographic printing. Gelatin plates, containing $K_2Cr_2O_7$, are exposed to light beneath pictures upon glass, and are then washed in water. The shaded portions soften and are easily removed, and leave behind a raised surface, which represents the lights. The plate so prepared is smeared with printers' ink, and impressions taken, as in lithography.

The plates used in instantaneous photography are gelatin "bromized" by long boiling with a solution of ammonium bromide, and subsequent treatment with silver nitrate.

Elastin is found, along with collagen, in all the elastic tissues, as in the arteries. It resembles albumin in its decomposition products.

Keratin forms the chief part of the epidermis, — nails, hoofs, horns, hair, wool, feathers, etc. It gives Millon's reaction, and dissolves in water heated to 200°, but it does not gelatinize upon cooling.

The two substances next described contain no sulphur, although in most other respects they resemble the other protein compounds.

Sericin ($C_{15}H_{25}N_5O_8$?), is obtained in solution when raw silk is boiled for some hours in water. It possesses the power of gelatinizing when present in so small an amount as one per cent. It is silk-gelatin. The portion of silk insoluble in water is *fibroïn* ($C_{15}H_{23}N_5O_6$?). It constitutes $\frac{2}{3}$ of the silk, and is the silk-albuminoid.

Nucleïn is found in the blood corpuscles of snakes, and is the basis of pus globules. It does not give the protein reactions, and is characterized by its resistance to the digestive ferments, dilute acids, and alkalies. It contains a notable amount of phosphorus, and may be regarded as a tetrabasic acid having the formula, $C_{29}H_{49}N_9P_3O_{22}$.

Cerebrin, $C_{57}H_{110}N_2O_{25}$, also occurs in pus corpuscles, but much more abundantly in brain and nerve substance. It may be extracted by hot alcohol, and obtained as a light powder, which readily absorbs water. It is an animal glucoside, from which an unfermentable sugar may be derived.

Recapitulation.

Groups of unknown molecular structure are provisionally classified:

I. Not containing nitrogen:

(1) As Bitter principles, like wormwood.

(2) As Glucosides, which decompose into glucose and these.

(3) As Indifferent bodies, like *cubebin*.

(4) Besides these, are anomalous bodies, like the bile constituents, and other non-nitrogenous animal secretions.

II. The Nitrogenous compounds, or albuminoids, are:

- (1) Albumins.
  - Sol. in H_2O. .
    - Albumin.
    - Casein.
    - Blood plasma.
  - The diffusible albumins: peptones.
  - Insol. in H_2O.
    - The globulins.
    - Lardaceïn.
    - The coagulated albumins.
    - Other derived albumins, as syntonin.
- (2) Gelatins . . . .
  - Collagen products—glue.
  - Chondrogen products—chondrin.
- (3) Nitrogenous substances related to these, the soluble ferments, the hæmoglobins, and hardened tissues, like skin and horn.

APPENDIX.

CRYSTALLOGRAPHY.

854. Solid bodies are either *amorphous* or *crystalline.* Amorphous bodies are those which have no well-defined geometrical form, as chalk, clay, starch. Crystals have regular, geometrical figures, bounded by flat surfaces called planes. Although the number of such figures is very great, it is possible to group them all into six primary forms, in each of which the bounding planes are supposed to be symmetrically disposed about imaginary lines called axes. These axes are generally three, which intersect each other in the center of figure.

I. *The isometric or regular system* has all the three axes at right angles to each other, and all equal in length. Such are the regular octahedra, represented by the alums; and the cubes, represented by common salt.

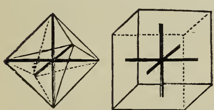

FIG. 109.

II. *The quadratic or tetragonal system* has all the three axes at right angles to each other; but of these, only the two lateral axes are equal in length. No cubes are possible in this system, but they are replaced by vertical square prisms. The octahedra of this system may have either form shown in Fig. 110, or the vertical axis may be shorter than the lateral axes.

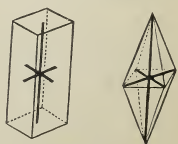

FIG. 110.

III. *The hexagonal system* has four axes. The three lateral axes are in the same plane, equal in length, and inclined to each other

at an angle of 60°. The vertical axis is perpendicular to these, and may be either longer or shorter than they. Neither cubes nor octrahedra are possible in this system. We may have six-sided prisms, like quartz; or rhombohedra, like Iceland spar.

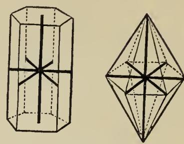

FIG. 111.

IV. *The ortho-rhombic or prismatic system* has three axes all at right angles to each other, but all unequal in length. Fig. 112 represents an octohedron of sulphur crystallized in the cold.

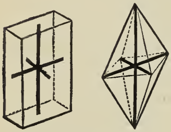

FIG. 112.

V. *The monoclinic system* has three axes which may all differ in length. The two lateral axes are at right angles to each other; the vertical axis is perpendicular to one lateral axis and oblique to the other. Sulphur crystallized after fusion, and sodium sulphate, are examples.

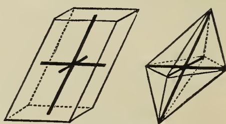

FIG. 113.

VI. *The triclinic or doubly oblique system* has three axes which are all unequal and obliquely inclined to each other. Such, for example, are crystals of cupric sulphate.

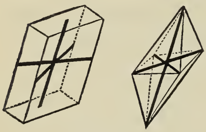

FIG. 114.

NOTE.—The student will do well to remember that these are the primary forms of crystals. The derived forms are so numerous that it would require a large treatise to describe them.

855. Some bodies crystallize in two forms, as sulphur. These are said to be dimorphous. When different bodies crystallize in the same form, they are said to be isomorphous. Such are the arseniates and phosphates of the same metal.

The word crystalline is often applied to bodies which are apparently made up of small interlaced crystals that can not be separated, but which are semi-transparent, as quartz rock.

PROBLEMS.

COMPARISON AT 29.92 INCHES (760 mm.) BAROMETER.

	32° F. = 0° C.					60° F.	
	WEIGHT OF 1 LITRE IN GRAMMES.	VOLUME OF 1 GRAMME IN LITRES.	SPECIFIC GRAVITY. AIR = 1.	SPECIFIC GRAVITY. H = 1,	WEIGHT OF 1 GALLON IN GRAINS.	WEIGHT OF 100 CUB. IN. IN GRAINS.	VOLUME OF 1 GRAIN IN CUB. INCHES.
AIR . .	1.2932	0.77	1.	14.43	71.604	30.954	3.23
HYDROGEN	0.0896	11.19	0.0693	1.	4.947	2.14	46.73
WATER .	at 4° C. 1000.	.001	773.2 at 15°C. 819.	11160.	pounds. 8.3456	25245.6 at 4° C. 25287.9	.00396

NOTE.—These problems are intended only as hints of work that may be done. The teacher may extend them indefinitely; and may add also such problems as involve specific gravity, specific heat, calorific power, etc. The problems are carefully graded; and if the student attacks them in the order given, he will find little difficulty in solving them. It is taken for granted that the bodies used are chemically pure, and that there is no loss in manipulation.

1. What is the weight of one cubic centimetre of each of the following substances, at the normal temperature and pressure?

(*a*) H; N; O; Air; Cl; CO; CO_2.
(*b*) H_2O; CS_2; H_2SO_4; HNO_3; Br.
(*c*) Li, K; Fe; Ag; Au; Pt.

What is the weight of one litre of each of the above? What is the bulk, in cubic centimetres, of one gramme of each of the above?

NOTE.—The Law of Charles is that *the volumes of all gases are proportional to their absolute temperature.* This temperature is reckoned from —273° C., and is therefore equal to their recorded temperature above zero + 273° C.; *e. g.*, the absolute temperature of air at 27° C. is 300° C.; and, at 127° C. is 400° C. Therefore, if a given weight of air measured one litre at 300° C., it would measure $\frac{400}{300} = 1.33$ L. at 400° C, absolute temperatures.

2. What is the volume of one cubic centimetre of the gases in Ex. 1, when reckoned at 100° C.? At 50° C.?

NOTE.—The Law of Mariotte is that *the volume of a gas is inversely proportioned to the pressure to which it is subjected; e. g.*, if a litre of air taken at a pressure of one atmosphere, or 760 mm. barometer, is subjected to the pressure of two atmospheres, it will be condensed to $\frac{760}{760 \times 2} = \frac{1}{2}$ of its former value; or, if the pressure is diminished to 570 mm., the volume will be increased to $\frac{760}{570} = \frac{4}{3}$ of its original volume.

3. What will be the volume of each of the gases in Ex. 1, when taken under a pressure of 1140 mm.? Of 380 mm.?

4. What will be the volume of each of the same gases reckoned at 100° C., and under a pressure of 950 mm. bar.?

5. What is the weight of each element in one gramme of H_2O? What is the bulk of each in this weight taken at 0° C.? What is the bulk of each taken at 100° C.? What will be the volume of the steam formed by their combination, (*a*) reckoned at 0° C.? (*b*) At 100° C.? How much pressure will be required to reduce the latter volume to the volume at 0° C.?

6. Given one gramme each of the following gases, HCl, H_2S, H_3N, CO_2, required—

(*a*) The weight of each of the elements forming these compounds. (*b*) The volume of each element. (*c*) The volume of the compound.

7. From the data given on p. 35, calculate how many cubic centimetres of water will be required to form a saturated solution containing one gramme of these gases. What will be the volume of the gas absorbed? What will then be the weight of the solution? Could the volume of the solution be calculated from the data given? Has the temperature or the pressure any effect upon the amount of the gas absorbed?

8. How many grammes of each element in 100 grammes of each of the following? H_2O; FeO; Fe_3O_4; Fe_2O_3; $FeCO_3$; $FeSO_4$; $FeSO_4, 7H_2O$. Are your answers percentages?

NOTE. — To calculate the empirical formula of a compound, (1) *find its percentage composition;* (2) *divide each constituent by its atomic weight;* (3) *reduce the quotients so obtained to their simplest ratios.*

9. Water yields in 100 parts:

			RATIOS.
H	$11.11 \div 1 =$	11.11	2
O	$88.88 \div 16 =$	5.55	1
	100.		

The formula is, therefore, H_2O. Calculate the formulæ from the following data:

(*a*)	N	82.35	(*b*)	Fe	70.
	H	17.65		O	30.
		100.			100.
(*c*)	K	28.73	(*d*)	Cu	57.46
	H	0.73		C	5.43
	S	23.52		H	0.91
	O	47.02		O	36.20
		100.			100.

10. How many grammes of Cu are required to make 100 grammes of Cu_2S; CuS; Cu_2O; CuO, $CuSO_4$; $CuSO_4, 5H_2O$?

11. If one gramme of K is taken, how many grammes may be formed of KI; KCl; HKO; $KHCO_3$; K_2CO_3; K_2SO_4?

12. If one gramme of zinc is taken to make hydrogen, (*a*) how much sulphuric acid will be required? (*b*) How much H will be liberated? Its weight? Its volume? (*c*) How much $ZnSO_4$ will be formed? (*d*) How much $ZnSO_4, 7H_2O$ may be crystallized out?

13. In making oxygen from K_2O, Cl_2O_5, what will be the weight of the products from 100 grammes? What, the volume of the oxygen?

14. Repeat these calculations with the reactions given for the manufacture of H_2S; CO_2; HCl; Cl; reckoning each as in Ex. 13 or in Ex. 12.

15. In the preparation of H_2O, N_2O_5 from 100 grammes of saltpeter, (*a*) how much H_2SO_4 is used when the salt remaining is $KHSO_4$? (*b*) How much when the salt remaining is K_2SO_4? (*c*) Suppose 147 grammes of H_2SO_4 were used, what would be the salt remaining? (*d*) Suppose that no loss occurred, what weight of nitric acid would be obtained? What volume? (*e*) Would there be any difference in these last two results whether 100, 150, or 200 parts of H_2SO_4 were taken?

16. How many grammes of FeS are required to form enough H_2S to precipitate 100 grammes of $CuSO_4$? Of $Bi(NO_3)_3$? Of $3H_2O, As_2O_5$? What will be the formula of the sulphides? Suppose the H_2S were passed into a solution of Fe_2Cl_6, how much sulphur would be precipitated?

17. Given this reaction, $2(PbO, N_2O_5) + K_2O, 2CrO_3 + H_2O = 2(PbO, CrO_3) + K_2O, N_2O_5 + H_2O, N_2O_5$, what will be the proportions taken and the products obtained? If one gramme of PbO, N_2O_5 is taken, what will be the weight of the others?

18. From the reaction given in § **212**, calculate how much of the two acids is necessary to dissolve one gramme of gold.

19. From the reactions in § **228**, calculate how much phosphorus can be made from 100 pounds of bone ash; then from 100 pounds of bones.

20. From the reactions given on p. 101, calculate the details of making 100 grammes of chlorate of potassa. (*a*) How much Cl is required? (*b*) How much NaCl? (*c*) How much H_2SO_4? (*d*) How much MnO_2? (*e*) How much KCl will be formed? (*f*) How can this last product be prevented from forming?

21. (*a*) How many cubic feet in a room 10 feet high, 15 feet long, and 12 feet wide? (*b*) How many cubic feet of oxygen does it contain? (*c*) How many pounds of burning charcoal will consume it completely, if it burns to CO_2? (*d*) How many pounds of burning charcoal will contaminate the air with five per cent of CO_2? (*e*) How long will it take one adult to contaminate it with two per cent of CO_2? (§ **302**). (*f*) How long will it take a gas burner consuming four feet of gas per hour to contaminate it with two per cent of CO_2? (*g*) How much fresh air should be admitted per hour so that, with the adult and the gas burner together, the air should not contain more than 0.5 per cent of CO_2? (*h*) Reckon the same from the size of your own bed-room.

22. Determine the atomic weight of chlorine from the following data: 100 grammes K_2O, Cl_2O_5 yield 60.939 grammes KCl; 22.032 grammes Ag (at. wt. 108) required 15.216 grammes KCl for complete precipitation (at. wt. $K = 39.1$), 14.427 grammes KCl gave 27.749 grammes AgCl.

23. 1.586 grammes pure Fe yield 2.265 grammes Fe_2O_3: calculate the atomic weight of iron.

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